June 1953 Pages 181 - 228

The Journal *of the* SOCIETY OF DYERS AND COLOURISTS

Volume 69 Number 6

CONTENTS

THE SOCIETY OF DYERS AND COLOURISTS 19 PICCADILLY BRADFORD YORKS

WAV

PAG

● FOR POLYMERISATION OF RESIN IMPREGNATED FABRICS

VY

GES

or

ng
elements as required

- Efficient and automatic temperature control — initial temperature quickly obtained
- Easy access with efficient insulation
- Compact and operative as a separate unit or part of a range
- Efficient air filtration
- Minimum length tension
- Versatile — water repellent and permanent glaze finish

THE MATHER & PLATT

BAKING STOVE

A FINE MACHINE...

Write now for details of the M & P Service to the Textile Trade

MATHER & PLATT LIMITED

PARK WORKS : MANCHESTER 10

A

A


PEGG
ESTABLISHED 1827
★ OVERFEED TO STRETCHER
★ FABRIC STEAMED ON STRETCHER
★ LARGE-DIAMETER COVERED BOWLS
★ NO WASTE AT END OF ROLL
★ SIMPLIFIED THREADING FROM FRONT OF MACHINE
★ NO BOWING OF COURSES
★ THREE-SPEED DRIVE
Built in 2 sizes
finished fabric widths up to 59"
The modern Horizontal Calender
gives Superb Finish to all classes of circular knitted fabrics
SAMUEL PEGG & SON · BARKBY RD · LEICESTER · ENGLAND
A COMPANY OF THE MELLOR BROMLEY GROUP
SP11


Mystox
for MILDEWPROOFING
and ROTPROOFING
COTTON · JUTE · FLAX etc.
Mystolene
for SHOWERPROOFING
ALL TYPES OF CLOTH PARTICULARLY
CARBONISED AND STRONG ACID DYED
PIECES, FIBRO MIXTURES, etc.
CATOMANCE LTD. · WELWYN GARDEN CITY · HERTS

MEMBERS' CHANGES OF ADDRESS

Broadhurst, R., formerly of Bolton, Lancs., to 39 Caledonian Road, Leeds 2

Butterworth, J. F. D., formerly of Davenport, Stockport, to c/o Westwood Inn, Featherstall Road, Oldham, Lancs.

Camidge, George M., formerly of 1 Monkbridge Avenue, Leeds 6, to 59 Troydale, Pudsey, near Leeds

Carlene, Dr. P. W., formerly of c/o Fibres Technical Service and Development Department, I.C.I. Ltd., to I.C.I. Ltd., "Gussens", Welwyn, Herts.

Clayton, Alfred, formerly of 2 Blenheim Mount, to 11 Heaton Grove, Frizinghall, Bradford

Crook, E., formerly of Radcliffe, to "Lyngwood", Falcon Road, Bingley, Yorks.

Crook, H., formerly of Bingley, to Dyestuffs Dept., Imperial Chemical Industries Ltd., Britannia House, Hall Ings, Bradford

Dean, H., formerly of Barrowford, near Nelson, to 64 Grange Road, Bury, Lancs.

Godrich, J., formerly of Sherstone, Staffs., to 31 Richmond Hill Road, Edgbaston, Birmingham 15

Grime, Miss S. M., formerly of Monton Green, Eccles, to 10 Wilton Polygon, Crumpsall, Manchester 8

Hardy, James, formerly of West Bar Chambers, Boar Lane, to British Ind. Solvents, 97 Vicar Lane, Leeds 1

Hartley, D. R., formerly of 4 Raleigh Street, Fenton Road, to 10a Thorn Tree Street, King Cross, Halifax

Henley, R. W., formerly of Bispham, Blackpool, to c/o 1 Victoria Street, Braintree, Essex

Heywood, J. V. A., formerly of Greenhill Road, Coalville, to "St. Helens", Warren Hills, near Coalville, Leics.

Kay, Eric A., formerly of Crumpsall, Manchester 8, to c/o Central Lab., The British Cotton & Wool Dyers' Assoc. Ltd., 22 Cumberland Street, Manchester 3

Kozubski, K. K., formerly of 3552 Shuter St., to c/o Ciba & Co., 1235 McGill College, Montreal, Quebec, Canada

Lipson, M., formerly of Box 19, Geelong, to 2 Montague St., Highton, Geelong, Victoria, Australia

Macleod, A. M., formerly of Giffnock, to 113 Beech Avenue, Newton Mearns, Scotland

Mason, J. G., formerly of Calcutta, to c/o I.C.I. (India) Ltd., Westcott Buildings, Kanpur, U.P., India

Mather, Wilfred, formerly of Milford, Co. Carlow, to St. Kilda, Sandycove Avenue East, Sandycove, Co. Dublin, Northern Ireland

Matchhar, B. S. I., formerly of Bombay, to Qv. No. 1, New Asstt. Line, Pirla Negar, Gwalior, N.B., India

Morrison, Robert E., formerly of Wilmington, Delaware, to c/o Leon Ferenbach & Sons, Wilkel Barre, Penn., U.S.A.

Pollitt, J., formerly of Salford 7, to 82 Baynorme Road, Higher Crumpsall, Manchester 8

Potempski, W., formerly of 25 Burns Street, to "Winslow", 76 Marshall Hill Drive, Mappersley, Nottingham

Satterthwaite, E. M., formerly of Queens Road, Leicester, to 64 Leicester Road, Thurceston, near Leicester

Sewell, Wm. G., formerly of Birmingham, to 2 Leyborne Park, Kew Gardens, Surrey

Thornton, P. W., formerly of 14 Fir Road, Paddock, to 10 Bank End, Nettleton Hill, near Golcar, Huddersfield

Tyler, A. G., formerly of Woodthorpe, to 43 Bennett Road Mapperley, Nottingham

Waldeck, W. S., formerly of Huddersfield, to c/o M. W. Morawicz (Apt. 1a), 4015 Maplewood Avenue, Montreal, P.Q., Canada

Wilson, G., formerly of Sowerby Bridge, to 2 North Royd, Hipperholme, Halifax

Zeldis, Leon, formerly of Philadelphia, Pa., U.S.A., to Condell 1228, Valparaiso, Chile, S. America

The Journal of the Society of Dyers and Colourists

(Subscription rates for non-members £4 per annum, post free)

(Abstracts section only printed on one side of paper— £1 10s 0d per annum)

NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1953 and pages 237–240 of the July 1952 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford, 1, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

Ancient and Modern Textile Production in London and the Home Counties — *E. Goodale*

The Search for New Dyes in relation to Modern Developments in the Textile Field (George Douglas Lecture) — *T. Holbro*

Radioactive Isotopes in Printing — *W. Meitner and H. B. Hampson*

Fugitive Tinting with particular reference to Celafibre — *H. C. Olpin and A. J. Wesson*

Fuel Efficiency in the Dyeing and Finishing Trades — *W. Short*

The Uses of Microscopy in Textile Dyeing and Finishing — *G. G. Taylor and J. C. Brown*

The Structure and Chemical Properties of Dyes in relation to their Use — *T. Vickerstaff*

COMMUNICATIONS

Polymerisation of a Series of Vinyl Monomers in Wool — *N. K. Boardman and M. Lipson*

Studies in the Fundamental Processes of Textile Printing.

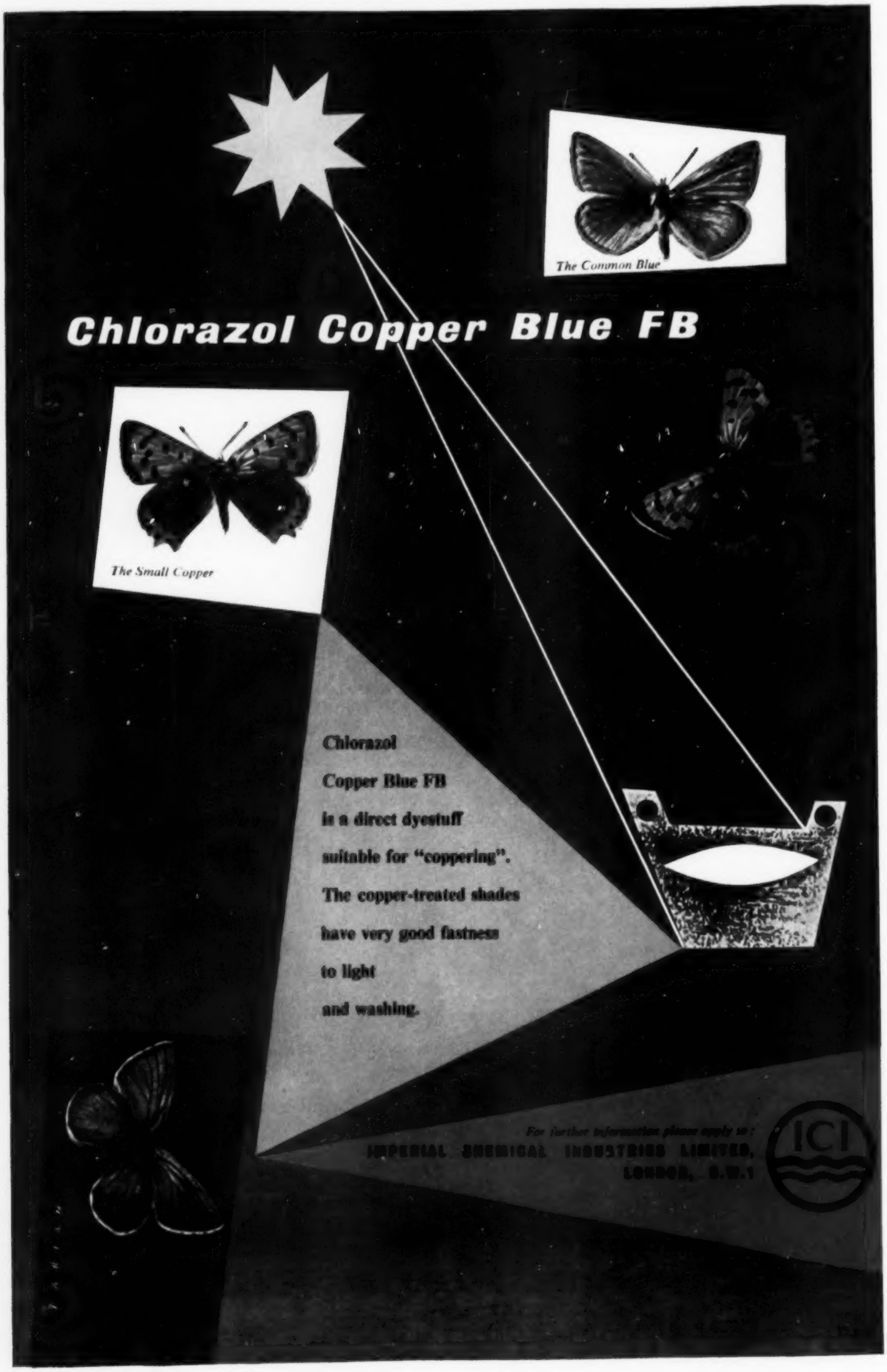
V— The Transfer of Disperse and Water-soluble Dyes to Cellulose Acetate during Steaming

VI— The Transfer of Disperse and Water-soluble Dyes to Nylon during Steaming

E. H. Daruwalla and H. A. Turner

Further Observations on the Effects of Evaporating Water from Cotton Cellulose — *G. W. Madaras and H. A. Turner*

The Use of Non-ionic Level-dyeing Assistants in Prechromed Dyebaths — *I. D. Rattee*



The Common Blue
Chlorazol Copper Blue FB
The Small Copper
Chlorazol
Copper Blue FB
is a direct dyestuff
suitable for "coppering".
The copper-treated shades
have very good fastness
to light
and washing.
For further information please apply to:
IMPERIAL CHEMICAL INDUSTRIES LIMITED,
LONDON, S.W.1
ICI

THE JOURNAL

OF THE

Society of Dyers and Colourists

Volume 69 Number 6 JUNE 1953 *Issued Monthly*

Proceedings of the Society

The Effects of the Soaping Aftertreatment on Vat Dyeings

H. H. Sumner, T. Vickerstaff, and E. Waters

Meeting of the Manchester Section held at the Gas Showrooms, Town Hall Extension, Manchester, on 15th February 1952, Mr. F. Farrington in the chair

The colour changes produced in vat-dyed cellulose fibres by the normal soaping aftertreatment have been examined quantitatively by spectrophotometric methods using dyed viscose film. From the increase in the orientation of the dye as shown by measurements of dichroism and from the analogous behaviour observed during the ageing of colloidal suspensions of vat dyes, it is concluded that the changes are associated with crystallisation of the dye. The efficiency of various soaping agents has been measured and also the effect of the temperature of the treatment, and it has been shown that soap and Lissapol N at the boil are the most efficient methods of treatment of those examined.

It has also been found that the effects observed on viscose film occur on normal commercial fabrics, although here the visual effect is diminished by the nature of the substrate and by the greater loss of dye which occurs in the soaping treatment owing to the greater relative surface area of fibrous materials. The light fastness of a series of vat dyes on cotton in the unsoaped and soaped states has been measured, and shows that soaping has, in general, little effect on light fastness. In those cases where changes are observed the effect may be either to increase or to decrease the light fastness according to the dye.

Introduction

The final stage in the dyeing of vat dyes is normally a treatment in a boiling solution of soap or other detergent. This aftertreatment has the double purpose of removing from the fibre loosely attached surface dye, thus achieving the full degree of fastness to washing and rubbing, and of effecting a colour change to the final stable shade. It has been known for some time that this latter change can be brought about by the application of wet heat in any form.

Various workers have examined this process in the past. Originally, it was thought that the change in colour on soaping was due to a completion of the oxidation process [1], but later work resulted in the suggestion that the colour changes were due to aggregation of the insoluble dye in the fibre [2]. Most of the earlier investigations were carried out, however, on azoic dyes, where closely similar effects are observed on soaping, and extended by analogy to the vat dyes. The general conclusions with azoic dyes are that heating under moist conditions causes aggregation of the pigment particles, which may in time proceed as far as actual crystallisation. The particles appear to migrate to the fibre surface and accumulate there in microscopic crystals, and it is this aggregation which gives rise to an increase in fastness to light and to a decrease in fastness to rubbing.

The first extensive experiments with vat dyes were carried out by Valkó [3], who investigated the colour changes of dyed Cellophane sheet on being soaped, and correlated these effects with X-ray measurements. The results indicated that the colour change was due to crystallisation of dye, and on the basis of his experiments Valkó classified vat dyes into three groups— (*a*) those which are amorphous both before and after soaping, (*b*) those which are amorphous before soaping and crystalline afterwards, and (*c*) those which are crystalline both before and after soaping. Most vat dyes fall into the second class, but it must be noted that, in contrast to the azoic dyes described above, the crystallites of vat dyes rarely reach microscopic size.

In order to explain the colour changes associated with this aftertreatment, earlier workers invoked the rule that, in a system which scatters light, the wavelength of the transmitted light moves towards longer wavelengths with increasing particle size. Unfortunately, the colour changes associated with soaping can be to either longer or shorter wavelengths depending on the dye; and furthermore, if such a mechanism were operating, the change of hue should continue with increasing time of treatment, whereas in fact there is a quite definite final hue. However, the failure of the light-scattering hypothesis to account for the observed facts does not eliminate crystallisation as the colour-changing factor. The light absorption of organic dyes is dependent on the electronic oscillations in the molecule, and if these oscillations are

modified in any way, e.g. by the bonding of the molecules to form a crystal lattice, then the compound can exhibit a different colour.

Summarising present ideas upon the colour changes which occur in the soaping of vat dyes, Kornreich concludes that these are due to crystallisation, the necessary preliminary being dispersion, and possibly hydration, of the dye. In this way the electronic oscillations of the molecule are altered to an extent which is expressed in the colour change [4].

The work described in the present paper was undertaken to confirm or disprove existing theories, and to extend the work of previous investigators by providing quantitative data on the effect of soaping over a wider range of vat dyes.

Experimental

To measure the changes in intensity and hue associated with the soaping of vat-dyed materials, spectrophotometric methods were used. As transmission measurements provide a more accurate and less ambiguous evaluation of the quantity of dye present than reflectance measurements, the various vat dyes were dyed on transparent viscose film (Diophane PT 300 of Transparent Paper Ltd.), and the absorption curves measured on the General Electric recording spectrophotometer or the Uvispek (Hilger) or Unicam (Cambridge) spectrophotometer.

To obtain an accurate comparison between the unsoaped and soaped films, very level dyeings were needed. These were obtained by dyeing the film for 5 hr. in test tubes fitted with ground glass stoppers, in which the film (approx. 0·5 g.) was placed in such a way as to avoid any folding or crinkling. In the initial experiments (Tables I and III) the conditions of dyeing were those recommended for the individual dyes. The concentrations of dye in the bath were adjusted to give dyeings of suitable strength for spectrophotometric measurement. In later work, when it had been shown that dyebath conditions had little or no effect on the property being measured, a standard dyebath (60 ml.) was used for all dyes, containing sodium hydrosulphite (4·25 g./litre) and caustic soda (1·7 g./litre). Dyeing was begun at 50°c. and continued for 5 hr., the dyebath being allowed to cool to room temperature over this period, and in this way satisfactory results were obtained. Purified dyes were used throughout this investigation except for the preliminary trials summarised in Tables I and III, where the ordinary commercial dyes were employed. All dyeings on the usual textile fabrics were carried out at the dyemakers' recommended temperatures and reagent concentrations. The aftertreatment, unless otherwise stated, was carried out in boiling soap solution (0·3%) for 30 min.

To examine the effect of soaping, the original dyed pieces were cut in two, one half being left untreated and the other soaped. The samples were prepared for measurement by trapping the wet film between microscope slides to ensure complete flatness, and also to eliminate any effects due to humidity or swelling. As the film dyeings showed anisotropy and as the optical system of the recording spectrophotometer employed polarised light, it was necessary to measure the absorption spectra of the films in two directions at right angles to one another, and to take the mean value in order to eliminate polarisation effects when using this instrument. The figures quoted in Table I are these mean values.

For an accurate evaluation of the dichroism of the dyes on viscose film (Table IV) the measurements were made on the non-recording instruments, using a Nicol prism attachment to give plane-polarised light, with the plane of polarisation at any required angle to the axis of extrusion of the film.

SPECTRAL CHANGES ON SOAPING

In order to obtain a general picture of the effects produced by soaping, a representative selection of vat dyes were first examined, unpurified dyes being used. Some typical results on viscose film are given in Fig. 1. It was found that not only does a colour change occur on soaping, but also marked changes in optical density occur, a fact which has not been commented upon by previous workers. Complete lists of the changes in peak wavelength and peak optical density are given in Table I, and it can be seen that nearly half the dyes show increases in

TABLE I

Changes in Optical Properties of Vat-dyed Films on Soaping

	Change in— Optical Density (%)	Peak Wavelength (mμ.)
Caledon—		
Pink RL	+125	−1
Yellow 3G	+45	+20
Brilliant Blue 3G ...	+40	−4
Red 5G	+35	+1
Red BN	+30	−2
Violet XBN	+30	−15
Jade Green XN	+30	−12
Gold Orange G	+30	−2
Blue RC	+25	−6
Brilliant Orange 6R ...	+15	+10
Yellow 4G	+15	+4
Yellow 5GK	+15	−3
Brilliant Blue RN ...	+15	−10
Red X5B	+15	+3
Brilliant Violet 3R ...	0	0
Dark Blue 2R	0	−27
Green 2B	0	−5
Brilliant Orange 4RN ...	0	−18
Orange 2RT	−5	−14
Brilliant Violet R ...	−5	+21
Brown 3G	−5	−2
Brilliant Purple 4R ...	−5	−4
Green RC	−5	+3
Brilliant Red 3B ...	−5	−5
Dark Brown 2G ...	−5	−2
Yellow 2R	−10	−4
Red 2G	−10	−5
Yellow GN	−10	−4
Yellow 5G	−10	−6
Green 7G	−10	−7
Gold Orange 3G	−20	−1
Jade Green 2G	−25	−12

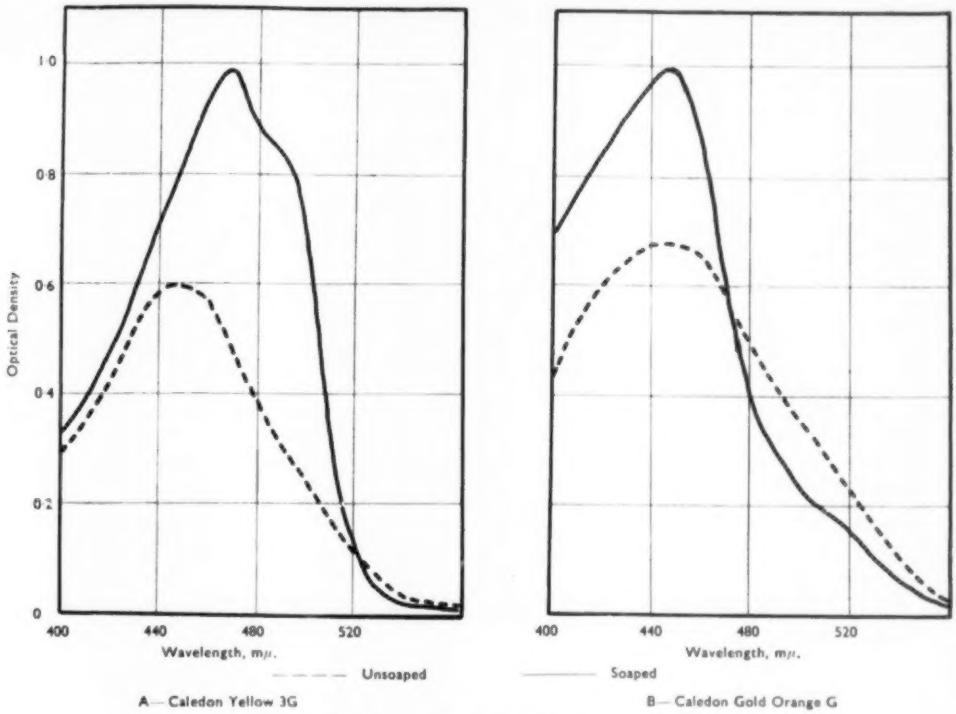


FIG. 1—Effect of Soaping on the Absorption Spectra of Vat Dyes

optical density, some of which are remarkably large. For example, Caledon Pink RL increases in optical density by 125%. These results are merely measurements of the optical density of the film, no account having been taken of the amount of dye lost in the soaping bath, and it may be, particularly with those dyes showing a small decrease in optical density, that the effect is due to this cause. A more detailed study of eight selected dyes involved stripping the film and estimating the amount of dye present before and after soaping, so that the extinction coefficient could be evaluated. These experiments showed that loss of dye into the soaping bath had occurred in certain instances, and after correction for this loss it was found that some of the dyes which previously had shown an apparent decrease now showed a much smaller decrease and sometimes even an increase in optical density

TABLE II

Changes in Optical Density and Extinction Coefficient of Vat-dyed Films on Soaping

	Change (%) in— Optical Density	Extinction Coefficient
Caledon—		
Pink RL	+125	+140
Yellow 3G	+45	+50
Brilliant Blue RN ...	+15	+40
Orange 2RT	−5	0
Green RC	−5	+5
Yellow 2R	−10	−15
Gold Orange 3G	−20	−5
Jade Green 2G	−25	+5

(Table II). The apparently anomalous behaviour of Caledon Yellow 2R is probably within the limits of experimental error.

THE DICHROISM OF VAT DYES ON CELLULOSE

The absorption of light by dyes is due to electronic vibrations induced by the light in certain linked systems of atoms in the dye molecule, which may be called *oscillators*. Any single oscillator must vibrate along a definite direction with respect to the dye molecule as a whole. Cellulose in all its forms shows molecular orientation to some extent, so that if a dye molecule is rigidly attached to the cellulose chain molecule it must partake of the original orientation of the cellulose. When a dyed film or fibre is examined in plane-polarised light, absorption of light can take place only if the electric vector of the light beam is in the same general direction as the oscillator in the dye molecule, and no absorption at all can take place when the two directions are at right angles. If an oriented cellulose film is dyed with a substantive and linear dye such as Congo Red and then examined in polarised light, the intensity of coloration is found to vary according to the angle between the direction of the cellulose (and also dye) molecules and the plane of polarisation of the light. In a very highly oriented sample, the dyed film may appear almost colourless when the electric vector in the polarised light beam is at right angles to the direction of extrusion of the sheet. Consequently, the variation in light absorption as the plane of polarisation is rotated relatively to the position

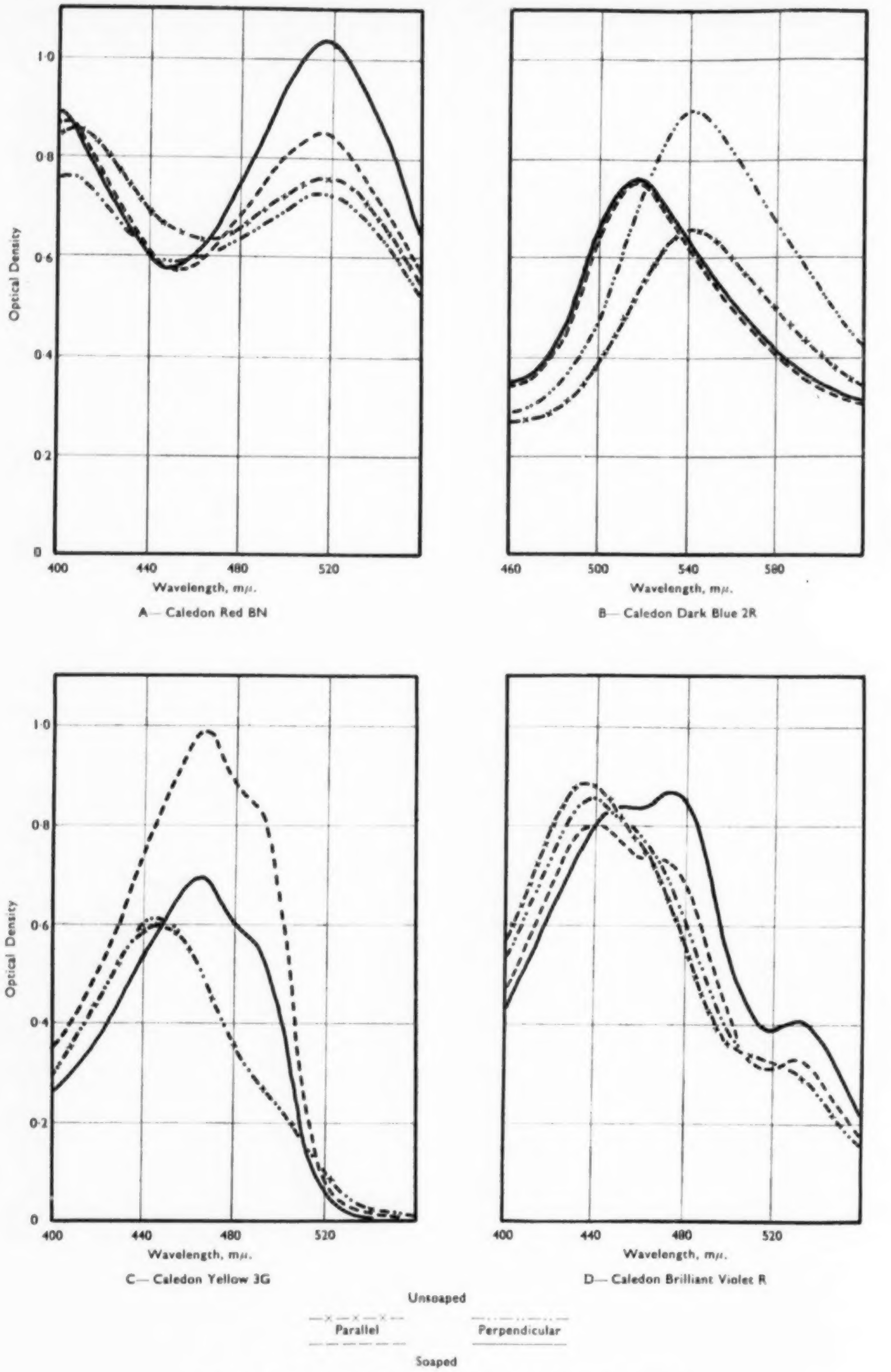


FIG. 2—Dichroism of Vat Dyes on Viscose Film before and after Soaping

of the film can be used as a measure of the orientation of dye molecules on that film or fibre.

In the case of direct cotton dyes, such as Congo Red, interpretation of the results is relatively simple, for the oscillator in the dye must consist of the conjugated chain of double bonds which run in a direction parallel to the length of this long, thin molecule. Furthermore, such a linear molecule is almost certainly adsorbed on cellulose parallel to the cellulose chains, so that the orientation of the dye is an indication of the orientation of the substrate. In the case of vat dyes, interpretation is more difficult, for the molecules are irregular in shape, and furthermore the electronic oscillators have not yet been clearly identified, so that the axis of the vibrations relative to the molecular structure is unknown. In addition some of the dyes show more than one absorption band and in certain cases the two oscillators responsible appear to lie along quite different directions in the dye molecule. In such cases the colour of the film in polarised light changes as the plane of polarisation is slowly rotated and so favours first one and then the other absorption band. An example of this behaviour is provided by Caledon Brilliant Violet R after soaping (Fig. 2D).

Qualitative measurements of this dichroic behaviour can be made very easily in the G.E. recording spectrophotometer, although this instrument is not ideal for the purpose, as the light beams are only partly polarised. However, this effect will merely reduce the magnitude of the dichroism observed, and will not affect the ranking of the different dyes nor the general conclusions which may be drawn. Complete absorption curves for four dyes on viscose film are shown in Fig. 2. It will be seen that Caledon Yellow 3G (Fig. 2C) shows no dichroism in the unsoaped state, but develops very marked dichroism on soaping, whereas Caledon Dark Blue 2R (Fig. 2B) behaves in exactly the opposite way. Furthermore, the shapes of the absorption curves for parallel and perpendicular orientation are very similar in the majority of the soaped dyeings. This constancy in the shape of the curve shows that the dye in the soaped state contains only one electronic oscillator contributing to the visible spectrum, and that the change in density in different directions relative to the film is due to the orientation of the dye, and not to the presence of a second oscillator. The molecules of Caledon Yellow 3G in the unsoaped condition must be randomly disposed, and the effect of soaping must be to render them mobile and enable orientation to take place. This is consistent with the formation of crystals in the fibre, and the very high order of the orientation further confirms this.

In order to obtain a more exact picture of the orientation, measurements on selected dyes were also made with plane-polarised light in one or other of the two non-recording spectrophotometers. The instrument was set at the wavelength of maximum absorption of the film, and the optical density determined at different angles of the plane of polarisation relative to the direction of extrusion of the sheet. In all cases the maximum density was found to occur when the polarisation was either parallel or perpendicular to the extrusion direction. No dye showing maximum density at a definite angle to this direction was discovered. Unfortunately, this does not necessarily prove that the electronic oscillator in the dye lies parallel or perpendicular to the cellulose molecules, for if in fact the oscillator lay at an angle and the dye molecules were randomly distributed in a radial manner around the cellulose chain, the total resolved vector of a large number of molecules would inevitably lie parallel or perpendicular to the cellulose molecules.

To derive from the dichroic measurements a quantitative figure for the orientation of the dye molecules in the film, it is necessary to adopt one or other of the arbitrary conventions which have been suggested [5]. In the present work it was decided to adopt the convention according to which the orientation in any direction is zero when the dye oscillators are oriented completely at random in space and is 100% when all the oscillators are parallel to the given direction. The amplitude of the oscillations in any molecule may be resolved into those of three oscillations at right angles, two in the plane of the dyed film, respectively parallel and perpendicular to the direction of extrusion, and the third at right angles to this plane. Unfortunately, it is impossible to make any optical measurements of this latter component, and so it has been assumed that it is equal to the perpendicular component in the plane of the film. This is equivalent to assuming that the distribution of dye molecules radially about the direction of extrusion is random. In actual fact it is probable that more dye molecules lie in the plane of the sheet than at right angles to it, but in the absence of experimental confirmation the above assumption is a first approximation to the true distribution.

If the optical densities measured with light polarised with the electric vector parallel and perpendicular to the direction of extrusion are denoted by $D_{\parallel}$ and $D_{\perp}$ respectively, then the orientation must be predominantly in the parallel direction if $D_{\parallel} > D_{\perp}$ and is numerically equal to—

$$\frac{D_{\parallel} - D_{\perp}}{D_{\parallel} + 2D_{\perp}} \times 100\%$$

If, on the other hand, $D_{\parallel} < D_{\perp}$, then the orientation is in the perpendicular direction and is equal to—

$$\frac{2(D_{\perp} - D_{\parallel})}{D_{\parallel} + 2D_{\perp}} \times 100\%$$

The orientation is doubled in this latter case, and the factor 2 is applied to $D_{\perp}$ in both denominators to take into account the assumption of random radial distribution of dye about the axis of extrusion.

The experimentally determined orientations calculated by means of these equations for the whole range of dyes before and after soaping are as shown in Table III.

When the first results were obtained covering soaping for 30 min. only, it appeared that the dyes could be divided into five groups having the following characteristics—

I— Disoriented before soaping; perpendicular orientation after soaping

II— Parallel orientation before soaping; perpendicular orientation after soaping

III— Parallel orientation before soaping; disoriented after soaping

IV— Parallel orientation before soaping; unchanged after soaping

V— Slight or no orientation before soaping; parallel orientation after soaping.

However, when further experiments were carried out on selected dyes, the time of the soaping treatment being extended, it became apparent that these groups were largely artificial and that only two types of behaviour were really significant. The major effect, observed with 28 out of the 32 dyes examined, is that the dyes pass from an orientation which is parallel to the cellulose molecules to an orientation at right angles to this. The inference is that the molecules are adsorbed from the dyebath in the reduced state alongside the cellulose molecules, and that on oxidation the attachment to the cellulose is destroyed and the molecules are then free to migrate and combine with one another to form crystals. Vat dye crystals are usually needle-shaped, and in the only case which has been studied in detail by X-ray analysis (indanthrone) the molecules are arranged across the length of the needles [6]. Hence, if the dyes form microcrystals on soaping, it is probable that the needles will lie along the direction of extrusion of the sheet, since the internal fissures in the sheet will lie in this direction, and consequently the molecules will be oriented at right angles to this direction.

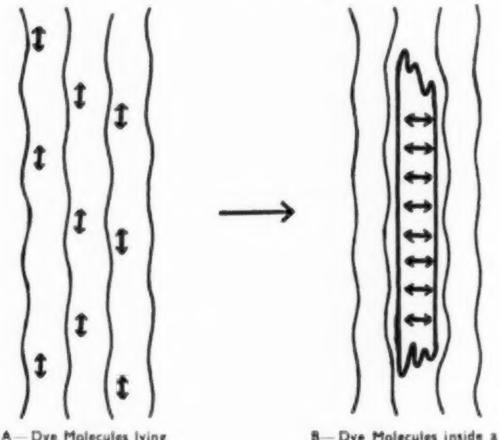
TABLE III

Orientation (%) of Vat Dye Molecules on Viscose Film before and after Soaping*

Time of soaping, hr. ...	0	0·5	5	8
Caledon—				
GROUP I				
Yellow GN ...	0	$16_{\perp}$	—	—
Yellow 5GK ...	$7_{\perp}$	$13_{\perp}$	$16_{\perp}$	—
Brilliant Orange 6R	0	$7_{\perp}$	—	—
Gold Orange G ...	0	$22_{\perp}$	$22_{\perp}$	—
Red BN	0	$13_{\perp}$	—	—
Red 2G	0	$22_{\perp}$	—	—
Red X5B ...	0	$7_{\perp}$	—	—
Brilliant Violet R	0	$7_{\perp}$	—	—
Violet XBN ...	$7_{\perp}$	$13_{\perp}$	—	—
Jade Green XN ...	0	$7_{\perp}$	$28_{\perp}$	—
Green 7G	0	$7_{\perp}$	—	—
GROUP II				
Yellow 5G ...	$7_{\parallel}$	$7_{\perp}$	—	—
Brilliant Red 3B ...	$7_{\parallel}$	$7_{\perp}$	—	—
Green RC ...	$4_{\parallel}$	$7_{\perp}$	$7_{\perp}$	—
Green 2B	$7_{\parallel}$	$7_{\perp}$	—	—
Blue RC	$4_{\parallel}$	$13_{\perp}$	—	—
Brilliant Blue 3G	$4_{\parallel}$	$7_{\perp}$	—	—
Brilliant Blue RN	$4_{\parallel}$	$13_{\perp}$	$22_{\perp}$	—
GROUP III				
Yellow 2R ...	$7_{\parallel}$	$4_{\parallel}$	$7_{\perp}$	—
Brilliant Orange 4RN	$4_{\parallel}$	0	—	—
Dark Brown 2G ...	$4_{\parallel}$	0	$7_{\perp}$	—
Brilliant Purple 4R	$4_{\parallel}$	0	—	—
Jade Green 2G ...	$7_{\parallel}$	$4_{\parallel}$	$13_{\perp}$	—
Dark Blue 2R ...	$13_{\parallel}$	0	$22_{\perp}$	—
GROUP IV				
Yellow 4G ...	$7_{\parallel}$	$7_{\parallel}$	0	$7_{\perp}$
Orange 2RT ...	0	0	$16_{\perp}$	—
Gold Orange 3G ...	$7_{\parallel}$	$7_{\parallel}$	0	$7_{\perp}$
Brown 3G ...	$4_{\parallel}$	$4_{\parallel}$	$(2_{\parallel})$	$(2_{\perp})$
GROUP V				
Yellow 3G ...	0	$19_{\parallel}$	—	—
Red 5G	$4_{\parallel}$	$19_{\parallel}$	—	—
Pink RL	0	$7_{\parallel}$	—	—
Brilliant Violet 3R	$7_{\perp}$	0	$4_{\parallel}$	—

* Dashes indicate that no measurements were made. Values in brackets are within experimental error.

The differences observed between the first four dye groups can be attributed to differences in the speed of crystallisation. Thus the dyes in Group I must crystallise rapidly, so that the initial parallel orientation has been lost in the oxidation process itself to give an unoriented dyeing before soaping; soaping for 30 min. then brings about the perpendicular orientation. In the Group II dyes, the initial parallel orientation is preserved during oxidation, but perpendicular orientation is rapidly produced on soaping. The Group III dyes are again slower to crystallise, and in 30 min. soaping crystallisation has gone only so far as to produce a substantially isotropic dyeing. On more prolonged soaping, however, further crystallisation occurs, leading to a definite perpendicular orientation. Slowest of all are the Group IV dyes, which in 30 min. soaping scarcely change from the original parallel orientation. Prolonged soaping for 5 or 8 hr. will, however, produce the perpendicular orientation even with these dyes. All these facts seem to fit well with the theory of crystallisation already outlined and illustrated roughly in Fig. 3.



A— Dye Molecules lying alongside the Cellulose Chains before Oxidation

B— Dye Molecules inside a Needle-shaped Dye Crystallite after Soaping

FIG. 3

Four dyes remain, however, which show exactly the reverse effect in that, on soaping, parallel orientation becomes more and more pronounced (Group V). In one case there is a definite change from an orientation which is originally perpendicular to a final parallel orientation. A possible explanation of this behaviour is that the oscillator system in these dyes is arranged at right angles to that present in the other dyes in relation to the

shape of the molecule or the way the molecule is adsorbed on cellulose. It may also be necessary to postulate that the oxidised dye crystallises in a different form or has a different crystal structure from the majority of the dyes.

If the postulates as to the rate of crystallisation are correct, then the dye should be in its most highly oriented form (with the oscillator parallel to the extrusion axis in the majority of cases) when it is adsorbed in the leuco state. Immediately on oxidation the changeover to the crystallised perpendicular orientation should begin. In order to support this hypothesis, dyeings of a number of the dyes in the leuco state and the same dyeings both before and after a normal 30-min. soaping were examined. In this case the manual spectrophotometers were employed to give a more accurate estimate of the dichroism. The results shown in Table IV, although not identical with those given in Table III, are in good agreement in all cases. It is perhaps noteworthy that in the cases of Caledon Yellow 3G and Caledon Pink RL there is now definite evidence of a perpendicular orientation before soaping, as would be expected from the explanation already suggested.

The data on the leuco dyes are difficult to correlate with those on the oxidised dyes, for in most cases the leuco dyes have two distinct absorption bands [7] which show different degrees of dichroism, and often the dichroisms of the two bands are at right angles to each other. This is shown quite clearly in Fig. 4, where the optical densities

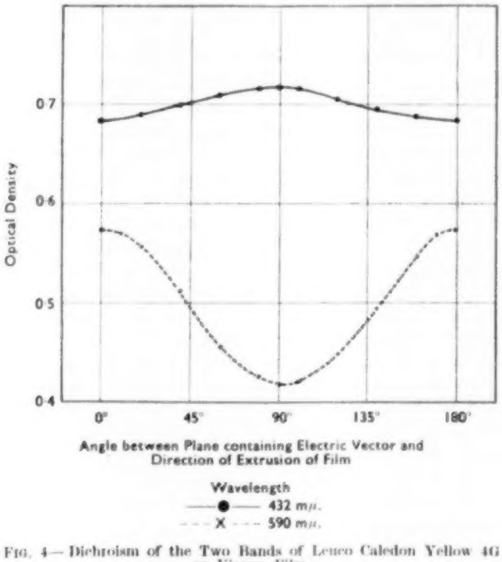


FIG. 4—Dichroism of the Two Bands of Leuco Caledon Yellow 4G on Viscose Film

of the two bands of leuco Caledon Yellow 4G are plotted as a function of the angle between the plane containing the electric vector and the direction of extrusion of the viscose sheet. It may be difficult at first sight to understand how two oscillators in the same molecule can give different orientation values, but this merely emphasises that the orientation so determined applies to the direction of the oscillator and not to the dye molecule as a whole. If the two oscillators are truly parallel then the orientations should be identical, and this is closely approached in Caledon Jade Green XN and Caledon Gold Orange G. As the angle between the oscillators increases so does the apparent discrepancy in orientation, and with an angle of 45° the orientation of one oscillator can be 0% when the other is 100%. A further complication arises from the fact that many of the dyes tested are benzamidoanthraquinone derivatives with considerable freedom of rotation around the amino grouping. If one oscillator is associated with this benzamido group, it is possible for it to take up an almost random orientation relative to a highly oriented anthraquinone nucleus. Finally, there is the difficulty that none of the absorption bands has

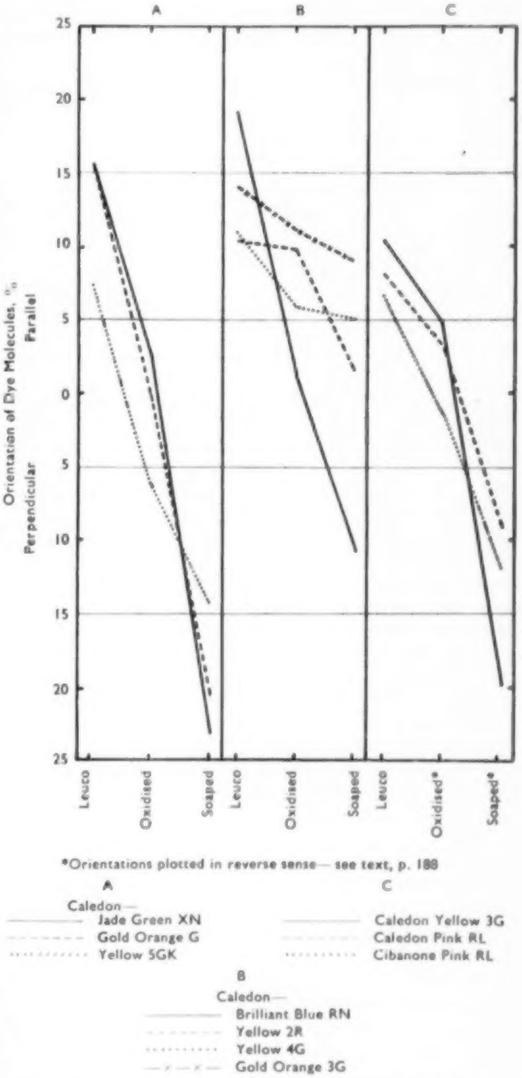


FIG. 5—Changes in the Orientation of Vat Dyes on Oxidation and Soaping

been associated with a grouping in the molecules, so that it is not possible to state which oscillator in the leuco molecule lies in the same direction as that in the oxidised dye or even whether there is any relation between the bands at all.

In spite of these difficulties it is possible to draw some definite conclusions from the figures in Table IV if attention is confined to that band in the leuco compound giving the maximum orientation. It will be observed that in all cases the numerical value of the orientation is higher for the leuco than for the oxidised state, which confirms that some disturbance of the original orientation occurs immediately on oxidation. Furthermore, in all cases, including even the Group V dyes, the direction of maximum orientation in the leuco dyeing is parallel to the direction of extrusion. If the orientation in the three states— leuco, oxidised, and oxidised and soaped— is plotted on an arbitrary scale as shown in Fig. 5, it will be seen that the changes are continuous and support the view that the unsoaped dyeing is merely an arbitrary stage in the process of crystallisation which begins immediately after oxidation and is completed by soaping. The slopes of these arbitrary curves (which may be regarded as approximate orientation–time curves) are in good agreement with the suggestion that Groups I–IV differ mainly in the rate of crystallisation. The dyes in Group V show a different behaviour, but if it is assumed that the oscillator in the oxidised dye is at right angles to that existing in the leuco dye, and the observed orientations in the oxidised form are plotted in the reverse direction, then these dyes also are seen to conform to the same pattern of continuous change and to fall into the class of rapidly crystallising dyes. Thus all the dyes examined appear to behave in a similar way if these suggestions are correct.

The orientation of some of these dyes in the leuco state is surprisingly high. For comparison, measurements made on dyeings on the same substrate with Congo Red gave an orientation of $15{\cdot}6_{\parallel}$, which was unaffected by pretreatment of the cellulose in a blank vat dyebath.

Another point of interest which may be derived from Table IV is that those dyes which show the greatest dichroism in the leuco state (Brilliant Blue RN, Jade Green XN, Gold Orange G) are all compact, rigid, fused-ring molecular structures, whereas the others all carry substituents of the benzamido type, capable of rotation, which presumably reduces the overall orientation of the molecules.

TABLE IV

Orientation of Vat Dyes on Viscose Film before Oxidation and after Soaping

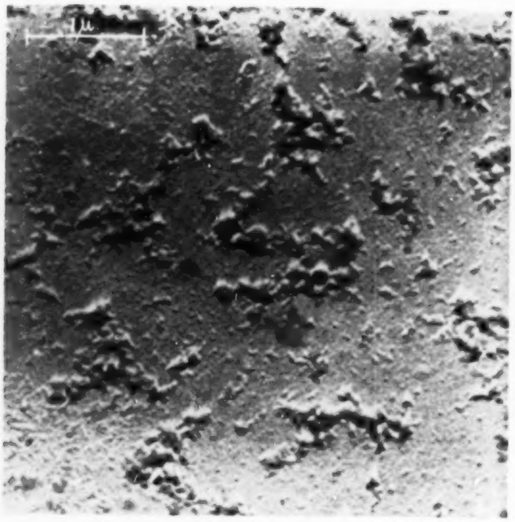
Dye	Orientation (%) of Dye Molecules in—			
	Leuco State		Oxidised State	
	Band 1	Band 2	Unsoaped	Soaped
GROUP I				
Caledon Jade Green XN ...	$15{\cdot}7_{\parallel}$ (625)*	$14{\cdot}8_{\parallel}$ (578)	$2{\cdot}7_{\parallel}$ (625)	$22{\cdot}3_{\perp}$ (615)
Caledon Gold Orange G ...	$15{\cdot}7_{\parallel}$ (556)	$14{\cdot}8_{\parallel}$ (520)	0 (450)	$20{\cdot}5_{\perp}$ (448)
Caledon Yellow 5GK	$7{\cdot}5_{\parallel}$ (559)	$2{\cdot}8_{\perp}$ (422)	$6{\cdot}1_{\perp}$ (414)	$14{\cdot}2_{\perp}$ (410)
GROUP II				
Caledon Brilliant Blue RN ...	$19{\cdot}3_{\parallel}$ (730)	—	$1{\cdot}3_{\parallel}$ (588)	$10{\cdot}6_{\perp}$ (584)
GROUP III				
Caledon Yellow 2R	$10{\cdot}5_{\parallel}$ (468)	—	$9{\cdot}9_{\parallel}$ (412)	$1{\cdot}6_{\parallel}$ (404)
GROUP IV				
Caledon Gold Orange 3G ...	$14{\cdot}1_{\parallel}$ (480)	—	$11{\cdot}1_{\parallel}$ (440)	$9{\cdot}1_{\parallel}$ (440)
Caledon Yellow 4G	$11{\cdot}0_{\parallel}$ (590)	$2{\cdot}8_{\perp}$ (432)	$6{\cdot}0_{\parallel}$ (442)	$5{\cdot}1_{\parallel}$ (449)
GROUP V				
Caledon Yellow 3G	$10{\cdot}5_{\parallel}$ (570)	$3{\cdot}0_{\parallel}$ (430)	$4{\cdot}9_{\perp}$ (441)	$20{\cdot}0_{\parallel}$ (463)
Caledon Pink RL	$8{\cdot}2_{\parallel}$ (598)	$5{\cdot}5_{\perp}$ (428)	$3{\cdot}4_{\perp}$ (514)	$9{\cdot}1_{\parallel}$ (514)
Cibanone Pink RL	$6{\cdot}9_{\parallel}$ (583)	$2{\cdot}7_{\parallel}$ (430)	$1{\cdot}3_{\parallel}$ (500)	$12{\cdot}0_{\parallel}$ (530)
Indigo	—	—	$6{\cdot}0_{\parallel}$ (660)	$7{\cdot}5_{\parallel}$ (660)

* The figures in brackets are the wavelengths of the absorption bands in mμ.

ATTEMPTS TO OBSERVE THE CHANGE IN CRYSTALLINITY DIRECTLY

The dichroism and absorption measurements have so far supported the concept of crystallisation on soaping, but additional, more direct evidence of the formation of crystals was felt to be desirable. Examination of the dyed films by optical and electron microscopy failed to reveal the presence of crystals. X-Ray analysis gave a slight indication of increased crystallinity on soaping in the case of Caledon Yellow 4G, but the increased sharpness of the diffraction pattern was extremely difficult to detect. Furthermore, the depth of this dyeing was far in excess of anything likely to be encountered in practice or in the other experiments, and any results which might have been obtained by loading the film still further with large quantities of dye in order to obtain crystals capable of X-ray detection could well be misleading. An alternative method of correlating the results with crystal growth was therefore sought.

To this end, the changes in the light absorption properties of colloidal solutions with time were examined. The colloidal solutions were prepared by oxidising normal leuco dye solutions very rapidly with acidic hydrogen peroxide containing Dispersol VL as dispersing agent. Optically clear solutions were obtained, which were examined spectroscopically after varying intervals of time. At each examination a sample of the dispersion was removed, immediately spray-dried, and examined



A— 3·5 min.

B— 13·5 min.

C— 128 min.

D— 91 hr.

Fig. 7—Changes in Particle Size and Shape with Time of a Colloidal Suspension of Caledon Pink RL

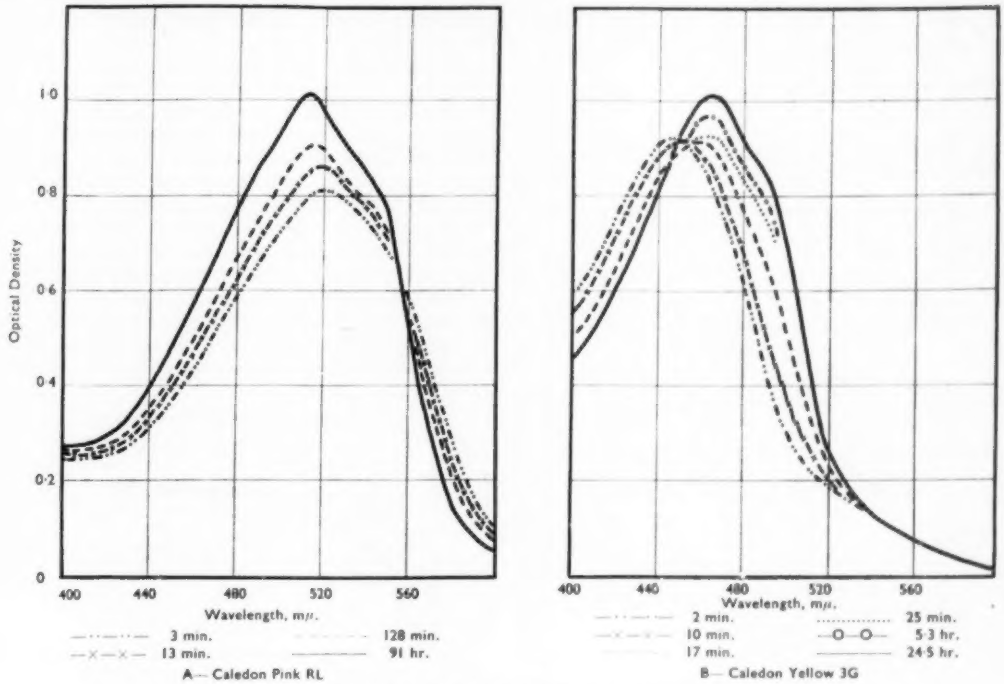


FIG. 6—Colour Changes associated with the Ageing of Colloidal Suspensions of Vat Dyes

in the electron microscope. In this way a series of curves was obtained for each dye (Fig. 6), which clearly showed, on comparison with the unsoaped and soaped curves for viscose film, that the changes in the colour of the colloidal solutions with time were similar to, although of smaller magnitude than, those occurring on soaping. Examination of the electron micrographs of the samples taken from these solutions after the same intervals (Fig. 7) showed considerable increases in the size of the crystallites. In the case of Caledon Gold Orange 3G, the colloidal solution showed no change in colour with time, and no change in crystal size. Also, to emphasise the similarity between these changes and those occurring on soaping, certain dyes, e.g. Caledon Yellow 3G, in which the change in light absorption occurs in two stages— firstly a change in peak wavelength, and then an increase in optical density (Fig. 2c)— gave exactly the same effect in colloidal solution. These observations seem to provide very strong additional evidence for associating the changes on soaping with the growth of dye crystallites in the fibre.

EFFECTS OF VARIATIONS IN THE DYEING AND SOAPING PROCESSES

So far the effects of constant conditions of soaping aftertreatments have alone been studied, and it is clearly desirable that the effects of varying these conditions should be examined. For this investigation purified samples of Caledon Pink RL and Caledon Yellow 3G were used, since these dyes showed marked changes on soaping. The effect of the concentration of dye on the fibre was first considered. Viscose films were dyed with increasing amounts of dye, so that the concentration of pure dye varied from 0 to 4% by weight. The actual dye concentrations (on both soaped and unsoaped patterns) were measured by stripping portions of the film with a Cellosolve–caustic soda–sodium hydrosulphite mixture, and estimating the concentration of the resulting solution spectrophotometrically. The optical densities of the films were measured on the Uvispek (Hilger) using unpolarised light at the peak wavelength. The results are shown graphically in Fig. 8. For each dye the dyed film obeyed Beer's law in both the unsoaped and soaped conditions, as is shown by the linear relationship between optical density and concentration, and the fact that the extinction coefficients are constant for all concentrations. This suggests that the physical form and size of the aggregates of both unsoaped and soaped dye are independent of concentration, as any changes would be reflected in changes in the light-absorbing properties of the material. Furthermore, the constancy of the ratio of the extinction coefficients of the unsoaped and soaped dyeings shows that the effect of soaping is independent of dye concentration. It is to be noted also that the soaped dyeings on the film, particularly of Caledon Pink RL, showed perceptible light scattering, which increased with concentration. This effect was quite marked when the film was viewed against a dark background, but was insufficient to make the film other than optically clear by transmitted light. This development of light-scattering on soaping, although obviously due to increased particle size, does not become noticeable at the same time as the changes previously considered. When the film is treated for varying

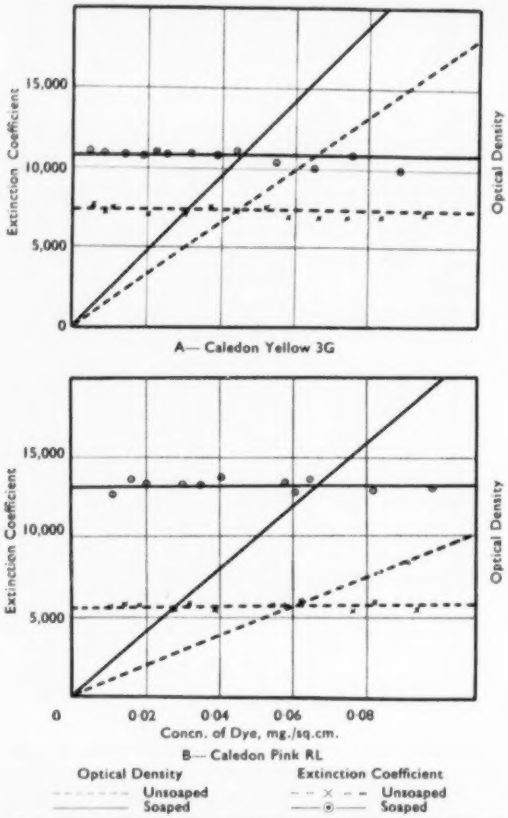


FIG. 8— Relation between Optical Density (and Extinction Coefficient) and Concentration of Dye on Viscose Film

lengths of time, the final colour and optical density are reached very quickly, and it must be assumed that this is due to crystallisation. On subsequent treatment the film remains at the same colour and density, but begins to scatter light, the intensity of which increases with the duration of soaping. This is presumably due to the crystallites of dye increasing in size until they attain dimensions suitable for light scattering. The particles in the dyed film at this stage must be approaching the wavelength of visible light, but have not become large enough to cause a decrease in optical density such as was observed in many of the colloidal solutions after a very long ageing.

To determine the effect of dyeing conditions upon the original unsoaped dyeing, and hence the effect upon the magnitude of the change associated with soaping, variations in the dyeing technique were made. These involved changes in the concentrations of caustic soda and sodium hydrosulphite, time of dyeing, and temperature of dyeing, and the addition of common salt and Dispersol VL to the dyebath. With the original dyeing as the control, the ratios of soaped to unsoaped optical densities on viscose film were compared and are listed in Table V. The ratio is practically constant for all the different dyeings of the two dyes considered, and it is evident that the dyebath conditions have little or no effect upon the physical form of the oxidised, unsoaped dyeing and hence upon the effects of soaping.

Of paramount importance in practice is the efficiency of any particular aftertreatment in developing the final soaped shade, particularly in continuous processes, where the time available may be very limited. With the object of measuring this efficiency, the rates of increase of optical density of films dyed with Caledon Pink RL and Caledon Yellow 3G were measured in different "soaping" media. The solutions used are listed in Table VI together with the results, expressed as the time required for the film to reach 50% of the final density figure, and the time required to complete the change. The actual rate curves are shown in Fig. 9. In general the same final optical densities

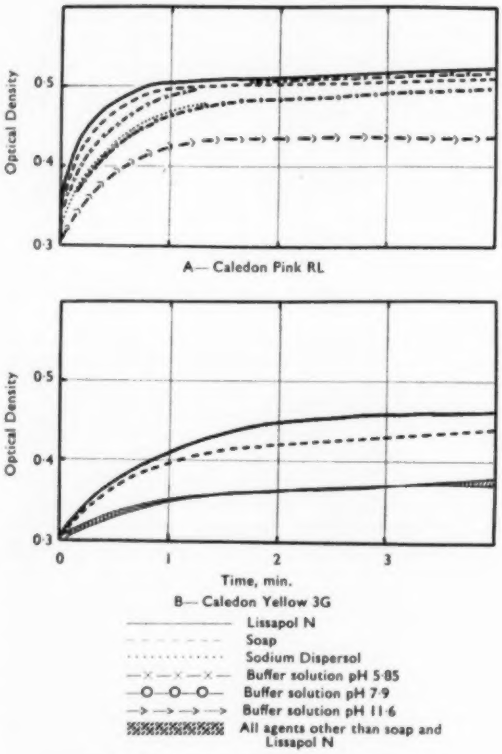


FIG. 9— Rate of "Soaping" with Various Agents

were reached in all the different media, except in the case of Caledon Pink RL in a buffer solution at pH 11·6, where very marked bleeding of dye occurs, resulting in a low final value. The results show that the dyeings of Caledon Pink RL change rapidly in shade and intensity in all aqueous treatments, no really significant differences in rates being observed. Caledon Yellow 3G, on the other hand, is generally much slower in development, and here the presence of detergent is obviously essential for an efficient treatment. When a detergent is present, the time required to complete the change in both cases is only small (6–7 min.) and approx. 90% of the change occurs within the first minute.

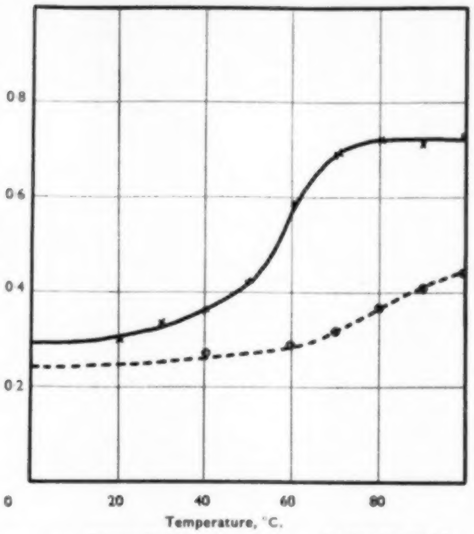


FIG. 10—Effect of Water Treatment of Vat-dyed Viscose Film for 1 hr.

However, probably more important than the duration is the temperature of soaping. Fig. 10 shows the effects of treatment in water for one hour at different temperatures, and here, again, the two dyes differ in behaviour. It can be seen that Caledon Pink RL is much more easily developed at low temperature, there being a critical region at 40–60°C., whereas the Caledon Yellow 3G slowly increases in rate of soaping up to the boil. At the boil both dyes rapidly develop their final shade. The practical inference to be drawn from these experiments is that most continuous processes should be capable of giving an efficient soaping, provided that, where the time available is limited, the temperature of the soaping baths is at a maximum.

TABLE V

Effect of Changes in Dyeing Conditions on Development of Shade on Soaping

(Normal dyeing carried out in a soln. containing 1·7 g. NaOH + 4 g. $Na_2S_2O_4$ per litre at room temp. for 5 hr.)

Change in Dyebath Conditions	Optical Density Soaped / Optical Density Unsoaped	
	Caledon Pink RL	Caledon Yellow 3G
Normal dyeing	2·45	1·52
Double caustic soda	2·31	1·56
Double sodium hydrosulphite	2·39	1·54
Dyed for 24 hr.	2·46	1·51
Dyed at 40°C.	2·10	1·48
Addition of sodium chloride	2·15	1·48
Addition of Dispersol VL ...	2·39	1·63

INFLUENCE OF SUBSTRATE

As explained on p. 182, dyeings on viscose film were used in all the work so far reported because of the advantages in convenience and accuracy of measuring the spectra and the changes therein. It is clearly of interest to enquire whether the results so obtained are applicable to normal textile substrates. At first sight such an extension would appear to be logical, but on the other hand the large increases in optical density (and so in apparent depth of shade) which are produced by soaping the films should be obvious on a textile fabric and yet do not appear to have been observed in practice. Accordingly experiments were carried out on a wider range of substrates to examine this point.

TABLE VI

Rate of Development of "Soaped Shade" in Various "Soaping" Media

"Soaping" Medium	Caledon Pink RL		Caledon Yellow 3G	
	Time (min.) till—			
	50% Change	Completion	50% Change	Completion
0·3% Soap solution...	0·2	7	0·6	7
0·3% Lissapol N ...	0·1	6	0·6	6
0·3% Sodium Dispersol	0·3	4	~7·0	>60
Buffer solution (pH 5·85)	0·1	7	~8·0	>60
Buffer solution (pH 7·9)	0·3	10	1·0	>60
Buffer solution (pH 11·6)	0·3	6	2·0	>20

In order to confirm in the first place that the effects of soaping are effective throughout the film and are not merely surface effects, dyeings on thicker film (600 quality) were examined and found to behave in an identical manner to the previous dyeings (300 quality film).

Experiments were next carried out on cotton, spun rayon, and Fortisan (Courtaulds) fabrics, and difficulties were immediately encountered owing to the much greater loss of dye from the fabrics on soaping, arising presumably from the greater surface area as compared with film, and also owing to the fact that the visual appearance of the fabrics (the apparent depth of shade) did not bear any simple relationship to the dye content.

A reflectance function has been derived by Atherton[8] which is applicable to the optics of the recording spectrophotometer, and which is a linear function of concentration. Linear curves are obtained by plotting this function—

$$\frac{1 - \frac{1}{2}R}{R}$$

(R = reflectance factor) against the concentration of dye on the patterns (Fig. 11). In the case of the cotton and Fortisan patterns the curves obtained for the soaped fabrics lie above those of the unsoaped materials, showing that the optical density of the dye in the fibre has increased. The constant slopes of the lines indicate that, as with film, the percentage increase of optical density on soaping is independent of dye concentration. The magnitude of the increase can be obtained for any fabric by direct comparison of the slopes of the soaped and unsoaped curves, and in neither case is the change as great as on film, as will be seen from Fig. 11. The dye concentrations plotted on the graphs were determined by stripping the dye from the patterns.

When the patterns were examined visually, however, no consistent differences in appearance were observed before and after soaping, and certainly no increase in apparent depth such as is indicated by the reflectance function–concentration

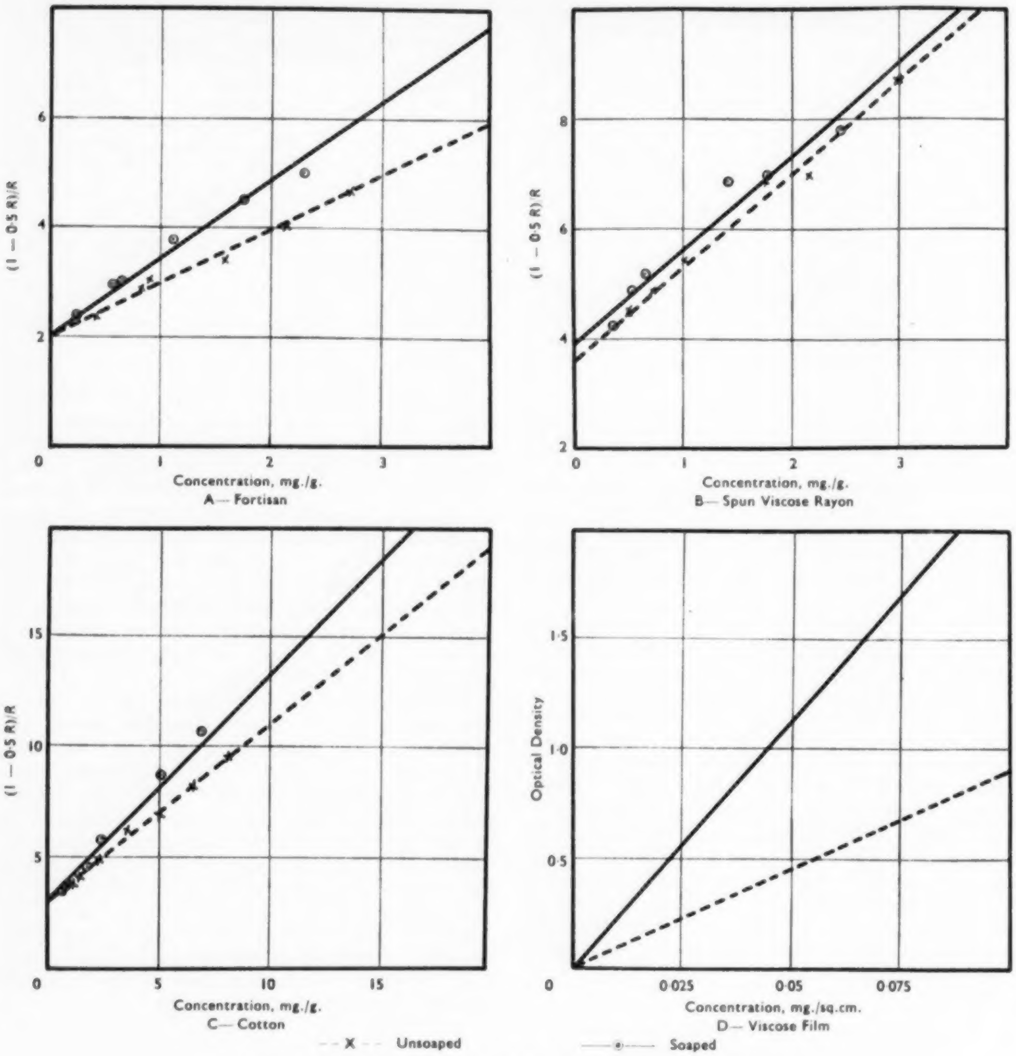


FIG. 11— Effect of Soaping on Caledon Pink RL dyed on Different Substrates

graphs. The explanation of this anomaly lies in the loss of dye from the fabric which occurs during soaping. In plotting reflectance function against concentration this loss is automatically taken into account, but when two samples of the same pattern before and after soaping are compared visually, then the increase in strength due to the crystallisation phenomena is more or less balanced by the decrease in strength due to loss of dye to the soaping liquor. Thus the weaker dyeings show a visual decrease in strength on soaping, and the heavier dyeings, where the bleeding is proportionately less, a smaller increase in strength than would be expected.

The dyeings on the heavy spun viscose fabric showed no increase in the reflectance function on soaping (Fig. 11) and so were visually weaker in all cases after soaping. This behaviour is particularly surprising, since viscose rayon is the most closely allied substrate to the viscose film of the earlier experiments. This effect may be related to the fact that the increases in the reflectance function of the cotton and Fortisan fabrics are less than on viscose film. In order to confirm this, the absorption coefficient of the dye in the fabrics was determined from the reflectance function. The results are shown in Table VII. It will be observed that the values obtained on the fabrics fall between the two limits set on film by the unsoaped and soaped dyeings respectively. The absorption coefficient of the dye in benzyl alcohol solution is still lower than in the unsoaped film, although quite close to it. Since the coefficient obtained in benzyl alcohol probably corresponds to the value for molecularly dispersed dye, while the higher values correspond to increasingly advanced stages of crystallisation, it appears that the dye on unsoaped film is almost molecularly dispersed, but

TABLE VII

Soaping of Caledon Pink RL on Various Substrates

Substrate	Ratio of Slopes $\frac{1-0{\cdot}5R}{R \times \text{Concn.}}$	Absorption Coefficient Unsoaped	Soaped	Ratio
Viscose film ...	—	15,500	37,500	2·42
Spun viscose rayon fabric...	1·00	24,500	26,000	1·06
Cotton limbric...	1·44	18,500	25,000	1·35
Fortisan fabric...	1·34	21,000	30,000	1·42
Benzyl alcohol...	—	14,500	—	—

that in the fabrics crystallisation has already proceeded to a considerable extent before soaping. This may be due to the retention of hot liquor by the fabrics when removed from the oxidising bath. The retention of water will be roughly in the order—viscose film $<$ Fortisan $<$ cotton $<$ spun viscose rayon, which is the same as the order of the ratios of the absorption coefficients before and after soaping.

This kind of effect might be expected to be particularly evident with Caledon Pink RL, which is sensitive at low temperatures (Fig. 10) and crystallises extremely rapidly (Fig. 9). Further changes on soaping with spun rayon fabrics might then be small and completely masked by bleeding.

EFFECT OF SOAPING ON LIGHT FASTNESS

Since the belief is generally held that soaping increases the light fastness of vat dyeings, a selected series of dyes on cotton were exposed to sunlight in both the unsoaped and soaped forms with a view to correlating the results with the effects already reported. After exposure, the patterns were examined for fading, and it was observed that the exposed portion of the unsoaped dyeings was similar in hue to the unexposed, showing that the physical form of the dye had remained the same despite the large amount of energy that must have been absorbed. The dye molecules must therefore have very restricted mobility in the dry fibre, and require the fibre to be in the wet-swollen state before crystallisation can take place. To assist in the comparison of fastness, the exposed unsoaped patterns were soaped, when their colour changed to that of the corresponding soaped and exposed patterns, and accurate strength comparisons became possible. The spectral curves (Fig. 12) were drawn for record purposes, and from these, quantitative measurements of the fading in just perceptible steps (N.B.S. units) were made (Table VIII). The only differences observed were that after soaping Caledon Gold Orange G was definitely faster and Caledon Jade Green 2G less fast, the measured difference in the other dyes being of a minor order and probably within experimental error. No explanation is afforded by the results previously obtained as to why these two dyes should behave in opposite ways. Both show an increase in extinction coefficient (Table II) and a change in dichroism (Table III) on soaping, the only difference being that the Green 2G is apparently much slower to change. By a similar argument, Caledon

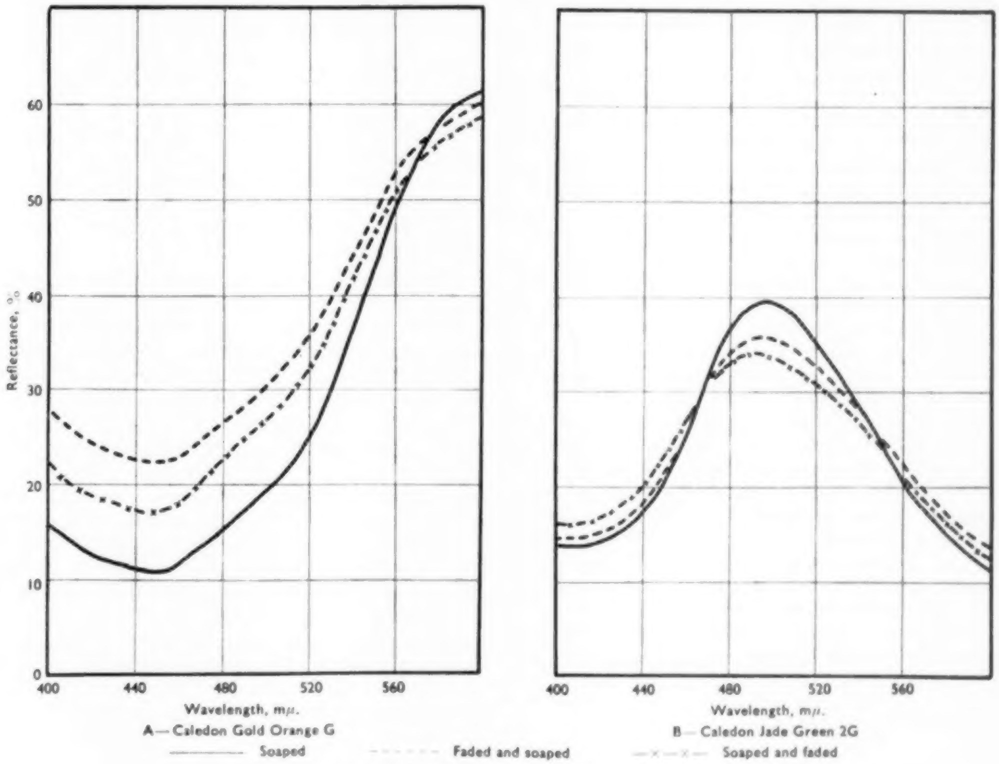


FIG. 12—Fading of Vat Dyes on Cotton Limbric

Pink RL would be expected to show marked differences in fastness in the unsoaped and soaped patterns, but this is not so. Thus, it would appear that the degree of crystallinity is not the controlling factor in determining light fastness, and equally that soaping does not serve the function of increasing the resistance of vat dyeings to fading.

TABLE VIII

Fading of Vat Dyeings on Cotton Limbric in Daylight

	Colour Difference (N.B.S. units) between Faded and Unfaded Patterns	
	Unsoaped	Soaped
Caledon—		
Gold Orange G ...	18	12
Orange 2RT	10	9
Jade Green 2G ...	3	9
Jade Green XN ...	6	5
Yellow 2R	6	5
Gold Orange 3G ...	7	8
Brilliant Violet 3R ...	2	2
Pink RL	4	5
Green RC	2	2
Brilliant Blue RN ...	2	3

Conclusions

The work reported in this paper upon the effect of the soaping aftertreatment upon vat dyes in cellulosic materials has increased the weight of evidence in favour of attributing the changes in colour to the effect of crystallisation of the dye within the fibre. The qualitative behaviour of the colloidal dispersions closely follows that of the vat dye dispersed in cellulose, and electron micrographs have shown that the changes here are accompanied by crystal growth. Similarly, the recorded changes in dichroism on soaping indicate very strongly that all the vat dyes are susceptible to this change on aftertreatment, the differences between dyes arising only from the rate at which crystallisation takes place.

Dyebath conditions do not influence the condition of the unsoaped oxidised dye, nor the degree of change on soaping, and neither does the concentration of dye in the fibre over a range applicable to practical dyeing. The rate of crystallisation can be extremely rapid even in water alone, but is improved by the addition of a detergent. The effect of temperature of soaping is more important than the time, and treatment at the boil is advisable when the time available is restricted.

The effects on commercial fabrics are not as great as those observed with film, probably because the practical conditions and nature of the fibre are more favourable to crystallisation occurring during oxidation. The visual effect is further minimised by loss of dye in the soaping bath, which is significant in the case of fabrics because of their high specific surface area. Soaping of vat-dyed cotton may increase or decrease the light fastness of the dyeings, but in general, with the dyes studied, appears to have little effect.

IMPERIAL CHEMICAL INDUSTRIES LTD.
DYEHOUSE LABORATORIES
HEXAGON HOUSE
MANCHESTER 9

(*MS. received 14th January 1953*)

References

1 Scholl, *Ber. dtsch. chem. Ges.*, **44**, 1448 (1911).
2 Bean and Rowe, J.S.D.C., **45**, 67 (1929).
3 Valkó, *J. Amer. Chem. Soc.*, **63**, 1433 (1941).
4 Kornreich, J.S.D.C., **58**, 177 (1942).
5 Preston, *ibid.*, **47**, 312 (1931).
6 Wells. Unpublished.
7 Waters, J.S.D.C., **66**, 544 (1950).
8 Atherton. Forthcoming publication.

Discussion

MR. H. A. TURNER: What is the mechanism by which detergent substances encourage the crystallisation of the dye during soaping?

MR. WATERS: In the growth of crystals some solubility in the medium is essential for transfer. It is therefore likely that the detergents, owing to their surface-active properties, have some dispersing or slightly solubilising effect on the finely divided particles which confers on the latter sufficient mobility to crystallise more readily than with water alone.

MR. F. CROMPTON: Can the very rapid crystallisation be slowed down advantageously?

MR. WATERS: We have not observed any retardation of crystallisation except that due to temperature. There appears no advantage in retarding the development of the true shade.

MR. A. S. FERN: Can the crystallisation of certain vat dyes be inhibited by the introduction of a small amount of another similar vat dye, perhaps as a shading colour?

MR. WATERS: We have not studied this aspect, but it is quite likely that crystal habit will be modified by the suitable addition of another dye or compound having the right molecular configuration. This is well known in other fields of crystallography, where *crystal modifiers* are encountered.

MR. R. L. HILL: Earlier work on the soaping of dyed materials, more particularly of natural cellulosic fibres, seemed to indicate that there was migration of the insoluble vat dye and aggregation in the region of the lumen. Do the present observations confirm this?

MR. WATERS: In all the microscopical examinations of the vat dyes we have been unable to detect particles large enough to be visible. There was no evidence of specific migration if judged by the intensity of colour in the lumen area of cotton or the outer surface of viscose rayon after soaping.

DR. P. W. CUNLIFFE: It is of interest to the warp dyer to note that the short time of soaping which he is able to give by this continuous dyeing method is sufficient for most vat dyes. Certain azoic combinations, however, require more time than is practicable in warp dyeing, and it would therefore be of interest to know whether any reagents have been found which are more effective than soap in accelerating the dye aggregation.

MR. WATERS: The only agent more effective than soap in promoting the crystallisation was Lissapol N. The difference was very slight, however, and it is not likely that significant practical advantages will accrue from selection of a detergent for speeding up the change of shade.

The Use of Hydrolysable Esters in the Control of Dyebaths

R. J. HANNAY and W. H. MAJOR

Meeting of the Huddersfield Section held at Field's Café, Huddersfield, on 18th November 1952, Mr. E. Rolfe in the chair

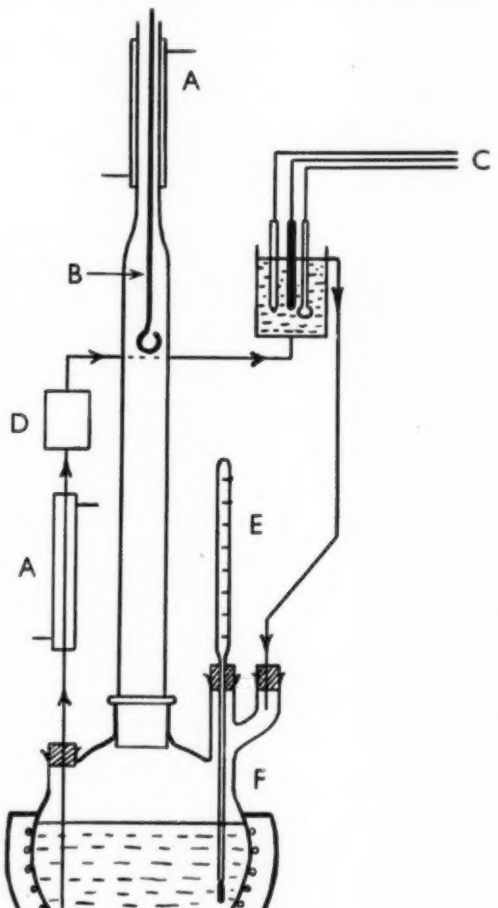
A study of the effects of initial pH, time, and temperature on the rate of hydrolysis of a number of esters in dyebaths is presented, and the results are discussed in relation to the selection of the most suitable ester to use under any particular set of conditions. It is shown that the hydrolysis of these esters is accelerated by raising the pH of the dyebath from 6 to approx. 10. In order to obtain the best results in the dyebath, an ester must be chosen the rate of hydrolysis of which is compatible with the time of dyeing under the particular pH conditions obtaining at the commencement of dyeing. The types of ester suitable for an initial pH of 6–7, 7–9, and 9–11 are indicated. This is followed by a survey of the experience gained in the use of these esters in wool dyeing on an industrial scale.

EFFECT OF pH ON HYDROLYSIS OF ESTERS

A study of the reactions which take place during the dyeing of wool by the metachrome process, undertaken during the latter part of 1951 and early in 1952, led to the suggestion that the use of certain hydrolysable esters in the dyebath would prove beneficial in promoting the level dyeing and good exhaustion of chrome dyes, and of neutral-dyeing acid dyes of the faster types such as the acid milling and Carbolan (ICI) dyes. The work was confined very largely to a detailed examination of the metachrome process[1], and much work remained to be done in investigating the effects of various dyebath conditions on the hydrolysis of the esters used and the effects on the resultant dyeings of the addition of these esters to the dyebaths.

A study of the effect of varying pH values of the dyebath on the rate of hydrolysis of a number of esters has been made, and it has been found that the initial pH of the dyebath plays an important part in determining the rate and extent of hydrolysis of the ester used.

A diagrammatic sketch of the apparatus used in these experiments, which were all carried out in the absence of wool, is given in Fig. 1. The electrically heated flask contained 600 ml. of a 0·067 M. phosphate buffer solution of the desired pH, and a metering pump circulated this boiling solution through a condenser, through a vessel containing a glass and a calomel electrode and the temperature compensator of the pH meter, and back to the flask. The pH of the cooled solution was continuously recorded; the interpretation of pH readings obtained in this manner has already been discussed[1]. When an ester hydrolyses in the boiling solution the change in pH which occurs will depend on two factors—(i) the amount of acid which is released by the ester, and (ii) the strength (pK) of the acid which is formed. The quantity of acid which is released depends on the proportion of ester which is added to the solution and on the degree of hydrolysis of this ester. Throughout the present experiments the amount of ester used was such that on complete hydrolysis the concentration of acid formed in the solution would be 0·025 N.



A Condensers
B Glass rod and hook
C To pH meter
D Metering pump
E Thermometer
F Electrically heated flask

FIG. 1—Apparatus for following Change in pH of Dyebaths

In a subsidiary series of experiments quantities of 0·067 M. phosphate buffer solutions were titrated with normal solutions of various acids and the changes in pH were followed. It was then possible to correlate a certain change in pH of a buffer solution with the addition of a known weight of a particular acid, and hence, in the rates-of-hydrolysis experiments, to determine at any time from the pH record the degree of hydrolysis of the ester. The curves reproduced in Fig. 2 and 3 were obtained in this way. Fig. 2 shows the effect of the initial pH of the solution on the rate of hydrolysis of diethyl tartrate. It will be seen that, whilst two hours' boiling resulted in some 60–80% hydrolysis at pH 7–8, only about 20% hydrolysis occurred in the same boiling time at pH 6. The

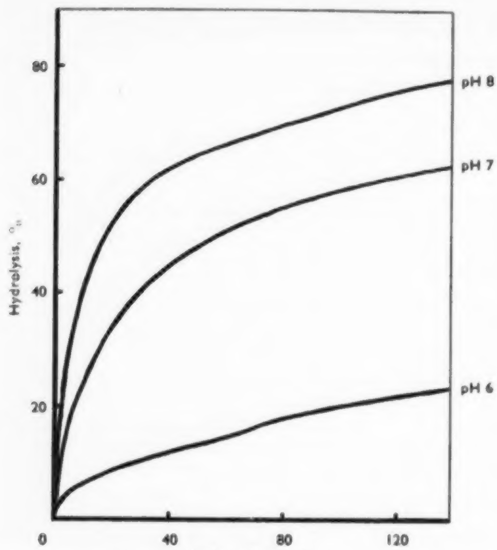


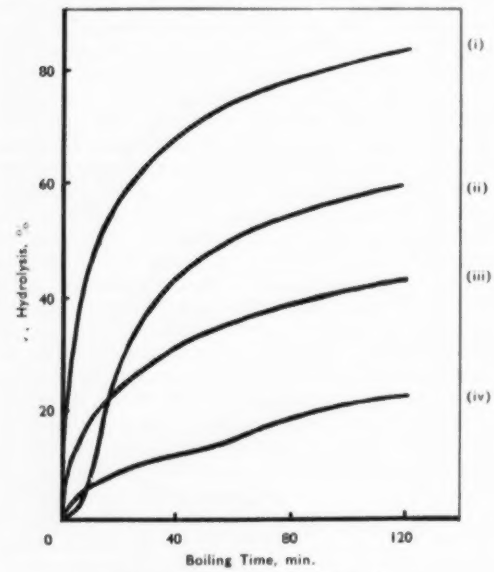
FIG. 2— Hydrolysis of Diethyl Tartrate (0·025 N.) in Boiling Phosphate Buffer Solutions (0·067 M.)

curves of Fig. 3 show how, under similar conditions, different esters hydrolyse at different rates, diethyl oxalate hydrolysing at approximately four times the rate of diethyl tartrate.

Fig. 4 and 5 show how the pH of a metachrome mordant solution containing—

Metachrome mordant	... ...	1·0 g.
1·5 N. Ammonium hydroxide	...	1·0 ml.
Distilled water, to make	...	600 ml.

changes with time during a typical process heating period. The pH measurements were begun when



(i) Diethyl oxalate (iii) Ethyl formate
(ii) Dibutyl oxalate (iv) Diethyl tartrate

FIG. 3— Hydrolysis of Esters (0·025 N.) in Boiling Phosphate Buffer Solution (0·067 M.) of Nominal pH 6

the temperature of the solution in the flask was 50°C. and continued as the bath was raised to the boil over a period of 45 min. and then kept for a further 90 min. at the boil. It will be seen that the extent and the rate of lowering of pH of the solution vary widely according to the ester used.

CHOICE OF ESTER

The significance of the effects occurring while the temperature of the bath is raised from 50°C. to 100°C. will be discussed later. The practical implication of these observations is that careful choice of the ester to be used has to be made, according to the conditions under which it is to be employed, if the most economic use and full value are to be obtained from the process. Whilst it has been observed that, in the dyeing of wool with the neutral-dyeing acid dyes and with many chrome dyes, the restraining effect of pH on the initial strike and levelling properties of the dyes works well at initial pH values between 7 and 8·9, and that under such conditions ethyl lactate and diethyl tartrate are probably the most suitable and economic esters to use, they are not the only esters which may be used. It is possible that for certain purposes a dyer may wish to begin dyeing at a pH either higher or lower than this limited range. For example, a specific enquiry was received concerning a dyebath the initial pH of which was to be 6. Although ethyl lactate or diethyl tartrate might serve quite satisfactorily under such conditions, it was felt that the slowing down of the rate of hydrolysis of these products by the lower initial pH of the bath might require an extended time of dyeing, or alternatively a loss in effectiveness of the ester owing to incomplete hydrolysis in the normal dyeing time. Therefore, it was suggested that dibutyl oxalate should be tried, as this ester has a similar speed of hydrolysis at an initial pH of 6 to those of the lactate and the tartrate at an initial pH of 8. If, however, the dibutyl oxalate were used in a dyebath of initial pH 8, the hydrolysis would be too rapid to yield the best results from a levelling point of view, although exhaustion of the dyebath would be satisfactory.

On the other hand, it has recently been suggested that, in the dyeing of nylon with certain types of dyes, the initial pH of the dyebath should be in the region of 10–11 in order to restrain the speed of "strike" of the dye, and that the pH should then be gradually reduced to about 4 to ensure exhaustion of the dyebath. In this case, if either ethyl lactate or diethyl tartrate were used at an initial pH of 10–11, the rate of hydrolysis would be too great to ensure level results. It is true that this effect might be counteracted by arranging a controlled drip-feed of ester to the dyebath, but this procedure has been avoided owing to the very real practical difficulties which arise in its effective control; such difficulties are accentuated when an attempt is made to adopt such a method in the actual addition of acid to a dyebath in the case of wool dyeing, owing to localised take-up of the acid by the wool. It is suggested that, in the case of dyebaths requiring initial pH values of the order of 10–11, such esters as triethyl citrate, diethyl succinate, and triacetin be tried. These have a

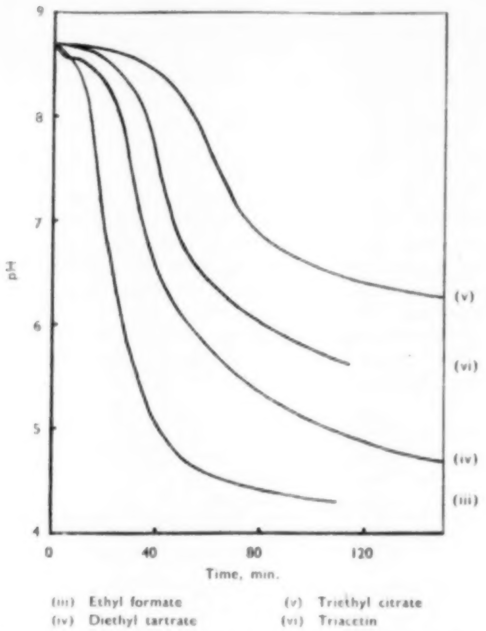


FIG. 4—pH of Metachrome Mordant during Hydrolysis of Added Esters (0·025 N.)

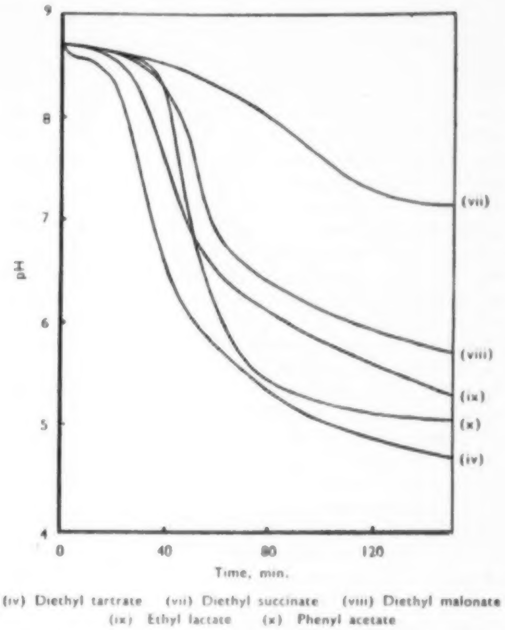


FIG. 5—pH of Metachrome Mordant during Hydrolysis of Added Esters (0·025 N.)

lower rate of hydrolysis than either ethyl lactate or diethyl tartrate at pH 8–9.

Another factor which has an important practical significance in the use of these esters in dyeing is the temperature at which appreciable hydrolysis begins. The ideal circumstance would be that no hydrolysis should take place until the dyebath reaches a temperature close to the boiling point, i.e. 97–100°C. Such conditions have not been attainable with esters which would subsequently hydrolyse at a suitable rate to fit in with normal dyeing times, but it has been possible to select esters which do not begin to hydrolyse until the temperature reaches approx. 80°C., and the amount of hydrolysis which occurs during the subsequent heating of the dyebath to the boiling point is small. It is thus possible to ensure that good penetration of a thoroughly mixed and homogeneous dye liquor is distributed evenly throughout the system before any appreciable dyeing takes place and before any significant lowering of the pH of the dyebath occurs. In this respect the following esters are typical examples of those which are suitable—triethyl citrate, ethyl lactate, diethyl tartrate, diethyl succinate, diethyl malonate, phenyl acetate, diethyl fumarate, dibutyl oxalate, and the mono-, di-, and tri-acetins. There is an appreciable variation in the speed of hydrolysis even in such a selection at any given initial pH, as will be seen by studying the rate of hydrolysis as indicated by the lowering of pH of baths containing metachrome mordant shown in Fig. 4 and 5.

By combining the properties relating to rate of hydrolysis with those discussed earlier in reference to initial pH, it is possible to select the most suitable ester for any set of conditions. For example, from the list cited above the following recommendations can be made—

(*a*) For baths with an initial pH of 6–7, dibutyl oxalate, diethyl fumarate, phenyl acetate, diethyl tartrate, and ethyl lactate may be used according to rate of hydrolysis required.

(*b*) For baths with an initial pH of 7–9, diethyl tartrate, ethyl lactate, diethyl malonate, triethyl citrate, diethyl succinate, and the mono-, di-, and tri-acetins.

(*c*) For baths with an initial pH of 9–11, diethyl succinate, triethyl citrate, and triacetin.

Such recommendations are made purely from a study of the rates of hydrolysis of the esters under varying pH conditions and do not take into account a number of other factors which are of importance to the practical dyer. Such factors as cost, availability, solubility in water, the relative strength of the acid released and its ability to reduce the pH of the dyebath, volatility of the acid produced, and the effect of the products of hydrolysis on the material being dyed and on the dyes being used—all have to be taken into account, but these factors do not affect the basic principle of the method put forward. At the present time the most attractive esters from the dyer's point of view are probably ethyl lactate, diethyl tartrate, dibutyl oxalate, and the acetins, but it must be borne in mind that with the development of the chemical industry, particularly in the past two decades, many products which were once looked upon as laboratory chemicals only have become in a comparatively short time cheap bulk products, and there is no reason to believe that this type of progress will not continue.

PRACTICAL DEVELOPMENT OF PROCESS

The practical development of the process in the dyeing industry during 1952 has been carried out almost exclusively with ethyl lactate and diethyl tartrate, although work is in progress with some of the other esters. At the time that the original paper [1] was presented, no results of bulk work done in the industry were available. Since then considerable experience has been gained in the practical application of the process to the dyeing of wool, and it is of interest to review the position in the light of the knowledge gained from this experience. The general position is that a number of works have tried out the process with considerable success, and it has been proved to be particularly successful in the dyeing of yarn both in the form of cheeses in circulating pressure machines and in hank form in machines of the Hussong type. It has also been used successfully in the dyeing of loose wool and wool tops. Trials have been carried out on cloth, but whilst these were quite good from a dyeing point of view, no definite assessment of the economic aspect of the process has yet been received in relation to piece goods. It must always be remembered that the technique does add to the cost of dyeing, and it is put forward, not as a general "cure-all" for dyeing troubles, but as a special process to enable dyers to produce consistent and level dyeings with certain dyes and classes of dyes which yield dyeings of high fastness properties but which present considerable difficulties to the dyer with respect to levelness and exhaustion. Several firms have already established the economic value of the process to themselves by careful selection of the particular dyeings to which they apply it.

The dyes which have been used in practice have all been either of the neutral-dyeing acid type or chrome dyes applied by the afterchrome or the metachrome process, and some interesting observations have been made relating to their application under bulk conditions. In the case of acid dyes of the fast milling and Carbolan types, it has been confirmed that the initial raising of the dyebath pH and the presence of a hydrolysable ester do restrain the initial rate of strike of the dye without reducing the percentage exhaustion of the dyebath at the end of the dyeing period, when compared with similar dyeings produced by either the ammonium acetate method or the Carbolan salt method. The extent of this restraining action is somewhat selective and varies with the dye used. In general, the action is most marked with those dyes which exhibit a high initial rate of strike and a high percentage exhaustion. Such selective action has been found to be very useful in the practical dyeing of mixtures of dyes which under ordinary conditions exhibit different rates of strike and exhaustion. The following example will illustrate this point—

Difficulty had been experienced in dyeing wool yarn with a mixture of 0·022% Carbolan Brilliant Blue 2RS and 0·018% Carbolan Violet 2RS by the ammonium acetate method, the results being unlevel. Dyeings produced from a bath containing 0·5% ammonia (25%) and 1% ethyl lactate were satisfactory. It was observed that until towards the end of the dyeing period the hues of the dyeings produced in the bath containing ammonia and ester were distinctly redder than those produced in the ammonium acetate bath, although the hues obtained on completion of dyeing were identical. The reason is that in the ester bath the rate of dyeing of the Carbolan Brilliant Blue 2RS, which is normally greater than that of the Carbolan Violet 2RS, is being restrained more than that of the latter dye and being brought more into line with the strike of the Violet, without the final exhaustion ratios of the two dyes being affected.

Other examples of binary mixtures of acid dyes which have been successfully applied by this technique are—

Carbolan Crimson BS (ICI)
Carbolan Violet 2RS (ICI)

Carbolan Crimson BS (ICI)
Carbolan Yellow 3GS (ICI)

Carbolan Green GS (ICI)
Carbolan Yellow 3GS (ICI)

Carbolan Brilliant Green 5GS (ICI)
Carbolan Yellow 3GS (ICI)

Carbolan Crimson 3B (ICI)
Alizarine Light Brown BL (S)

Brilliant Alizarine Milling Blue BL (S)
Lissamine Ultra Sky RS (ICI)

Fast Jasmine G (Gy)
Sulfonine Yellow CSR (S)

The mixtures containing Carbolans have been applied in bulk to loose wool stock, carbonised loose wool stock, worsted yarn in cheese form, botany yarn in cheese form, and woollen yarn in cheese form, whilst the other mixtures were applied to the yarns in cheese form. All the results were satisfactory, and a great improvement on those which had been obtained previously. The amount of ammonia (25%) used has varied between 0·5% and 1% and the amount of ester between 1% and 2·5% according to the depth of dyeing and the dyes used, and no other additions have been made to the baths. Good exhaustion of the dyebaths and level dyeings have been obtained with both loose wool and yarn.

With chrome dyes the technique has been applied to both the afterchrome and the metachrome processes. In the former case the actual dyeing follows the pattern of the acid dye process, but in the metachrome process the sequence of reactions is more complicated and not so easily followed. The levelling effect has been obvious in the finished goods, but the restraining effect on the speed of dyeing has not been so noticeable. In the laboratory we have not been able to note any slowing down of exhaustion in the metachrome process, and in some cases there appears to be a slight acceleration. In spite of this, metachrome dyeings in bulk with the addition of ethyl lactate and diethyl tartrate have shown much improved levelness. It is possible that the effect in this process is linked up with the speed of chelation of the dye and mordant, a slowing down of which may allow some migration of the dye before lake formation takes place. The conditions in the metachrome

dyebath are quite different from those in an ordinary neutral bath for acid dyes, in that alkali is produced by the reaction of the mordant with the wool and the pH of the dyebath tends to rise during dyeing. This in turn could be expected to slow down the rate of dyeing, giving an effect similar to that produced by the addition of ammonia to the neutral dyebath. As metachrome dyebaths are normally alkaline at first, the addition of ammonia does not display such a noticeable effect on the earlier stages of dyeing as in the case of a neutral dyebath, but with a hydrolysable ester present in the dyebath the addition of ammonia has been shown to be necessary to obtain the best results. The effect of the ester, as pointed out in our original paper [1], is to prevent any rise in the pH of the metachrome dyebath during dyeing, and this could be expected to assist exhaustion of the dye. It would appear, therefore, that in the case of metachrome dyeing there are additional factors coming into play which may be connected with the mechanism and the rate of formation of the metal-dye complex.

Some examples of chrome dyes which have been successfully applied by this technique in the dyeing industry are—

Metachrome Brown B (Br) Metachrome Orange R (Br)	Dyed on worsted hanks in a Hussong machine
Metachrome Olive 2G (Br)	Dyed on crossbred tops in a circulating pressure machine which was fitted only for one-way circulation
Solway Blue Black B (ICI)	Dyed on botany yarn as a grey in cheese form
Eriochrome Brown DKL (Gy) shaded with— Metomega Chrome Green GL (S) Sulfonine Yellow CSR (S)	Dyed on worsted yarn in cheese form
Synchromate Red BNL (Ciba) shaded with— Eriochrome Bordeaux C2B (Gy) Solway Blue Black B (ICI)	Dyed on worsted yarn in cheese form
Deep bottle green (dye not specified)	Dyed on loose wool by the afterchrome process

Two points of interest common to both acid dyes and chrome dyes have arisen in connection with the application of the ester technique. The first relates to the temperature of the bath at which dyeing is begun. The recommendation which has been made is that dyeing should be started at 50°C. and that the bath should then be raised to the boil over a period of 30–45 min. Some dyers, however, have been accustomed to using the Goodall technique [2], in which dyeing is commenced at the boil, and the question has been raised as to whether this technique is suitable when a hydrolysable ester is present in the bath.

The answer to this question is closely linked to the work described in the earlier part of this paper on the rate of hydrolysis of the ester in the dyebath. Theoretically, if an ester is used which shows no signs of hydrolysis until a temperature of 100°C. is reached, there would be no objection to commencing dyeing at the boil, provided the subsequent rate of hydrolysis was of the correct order. In practice, however, it has been found that hydrolysis does begin slowly at temperatures somewhat below boiling point, and therefore it is advisable to commence dyeing at temperatures below that at which any appreciable hydrolysis occurs. The purpose of raising the initial dyeing temperature to the boil is to improve levelling and bring about maximum molecular solution of a number of dyes of the neutral-dyeing non-levelling type. With many of the newer and faster types of dyes the advantage of such a procedure is doubtful. For example, with the Carbolan dyes no advantage has been found with this method, and in the makers' instructions for the dyeing of the recently publicised Cibalan (Ciba) and Irgalan (Gy) dyes it is strongly recommended that dyeing should be started at 60°C. and not at the boil. It may be that in some specific instances our recommended initial temperature of 50°C. is rather too low, owing to aggregation of the dye molecules in solution at this temperature, in which case the initial dyeing temperature has been raised from 50°C to 70°C., but it is not recommended that this latter temperature be exceeded, and in most cases tried in bulk under works conditions the recommended initial temperature of 50°C. has proved to be satisfactory.

The second point relates to the final exhaustion of the dyebath, and was first raised by Dr. J. F. Gaunt during the discussion on our original paper [1]. He stated that with a number of fast acid dyes the use of diethyl tartrate alone would not give satisfactory exhaustion of the dyebath and that in order to obtain maximum exhaustion it was necessary to add either Glauber's salt or acid. We have confirmed that the presence of a neutral salt such as Glauber's salt in the dyebath does not affect the normal progress of pH control by the ester, but obviously the addition of acid to the bath is tantamount to a lowering of the pH and would present the practical difficulties of control previously referred to [1]. This question of satisfactory exhaustion is one which up to the present has not been met in any works-scale trials which have been carried out, as in every case satisfactory exhaustion has been obtained even when the final pH of the dyebath has been slightly higher than that obtained when the ester technique is not used. Two alternative suggestions may be made to deal with such a case should it arise—It is probable that a dye which requires a pH of 4–5 to give satisfactory exhaustion will not require an initial pH of 8 in order to restrain the initial strike sufficiently to obtain level results, in which case an initial pH of 6–7 might be tried, and diethyl tartrate or ethyl lactate be replaced by an ester such as dibutyl oxalate. This would produce a rate of hydrolysis comparable to that of the two latter esters at the higher pH of 8 and yield a final pH in the region of 4·5–5, which in turn should give better exhaustion of the dyebath. If, however, it is found that a higher initial pH is still required to produce a satisfactory restraining action on the dye, or if the dye is to be used along with other

dyes which require the higher initial pH, then it is suggested that Glauber's salt be added towards the end of the dyeing period to produce a salting-on effect similar to that obtained in the dyeing of direct cotton dyes on cellulose. The Glauber's salt may be added at the commencement of dyeing, but there is always the danger of producing aggregation of the dye in solution and bringing about the salting-on effect too early in the dyeing cycle.

Recently, some very interesting work has been published on the effect of the addition of three ammonium salts—ammonium sulphate, ammonium phosphate, and ammonium acetate—to dyebaths containing wool[3], from which it is concluded that for controlling the pH of slightly alkaline or neutral dyebaths ammonium acetate is the best salt to use. We feel that this conclusion is fully justified by the results given when dyeings of some of the newer fast acid types of dyes produced from baths containing these three salts are compared, but it has been found that the levelness of dyeings produced even with ammonium acetate is not always satisfactory, and still better results have been obtained by the ester technique. This is definitely the case with the Carbolan dyes. Some work has been done on the dyeing of Irgalan and Cibalan dyes, which are among the most level-dyeing types of the newer fast acid dyes for wool, though comments from the trade have indicated that under certain conditions they are not completely satisfactory. Dyeings produced in the laboratory have shown that satisfactory results may be obtained by the use of diethyl tartrate or ethyl lactate, but it has been difficult under laboratory conditions to assess the extent of the improvement, particularly in relation to levelness, as no really unlevel results were obtained when a straightforward neutral-dyeing technique was used, in this case without addition of any ammonium salt to the dyebath. The final exhaustions of the dyebaths containing ammonia and ester were, however, rather better than of those without these additions. Nevertheless, a report from one dyeing firm confirmed that better results were obtained by the use of diethyl tartrate and ammonia than by the recommended technique in some bulk trials with the Cibalan dyes on yarn. Work is also proceeding on the use of these esters in the dyeing of nylon, and it has been found that the technique can be successfully applied in this direction. Here, again, it has been stated that superior results were obtained in the dyeing of Solochrome Brown RH (ICI) on nylon by using ethyl lactate instead of ammonium acetate.

The results obtained both in the laboratory and under works conditions indicate that the use of hydrolysable esters in the control of dyeing is of more than academic interest and provides a means of obtaining improved results under what are normally difficult conditions. Patents have been applied for covering the use of such esters in dyeing, but the esters have been made freely available to the industry under the registered trade name of *Estrocon* and the process has become known as the *Estrocon process*.

* * *

Finally, grateful acknowledgment must be made for the co-operation and help received from a number of firms in the dyeing industry in the commercial development of the process. The authors' personal thanks are due to a number of colleagues for work carried out by them which has made possible the presentation of this paper, and to the Directors of Messrs. Brotherton & Co. Ltd. for permission to publish it.

(MS. received 28th November 1952)

References

[1] Hannay, Major, and Pickin, J.S.D.C., **68**, 373 (1952).
[2] Goodall, F. L., *ibid.*, **54**, 45 (1938).
[3] Grundy, *Dyer*, **108**, 685 (14th Nov. 1952).

Discussion

ANON: Have the authors had any reports on the use of hydrolysable esters in the dyeing of wool piece goods with Carbolan dyes?

Mr. HANNAY: No reports on the dyeing of piece goods specifically relating to Carbolan dyes have been received. The method has been tried in bulk with piece goods, but beyond a statement that satisfactory dyeings have been produced, no further information has been received up to date and it is not known what dyes were used in these trials.

Mr. G. K. SEDDON: Does use of the ester technique alter the fastness properties of certain dyes?

Mr. HANNAY: No. However, application of a metachrome dye to a chrome-mordanted yarn in order to obtain a satisfactorily level dyeing resulted in a slight reduction in milling fastness, which gave trouble owing to staining when pieces woven from this yarn, together with white yarns, were milled and finished. When the ester technique was adopted, this dye gave satisfactorily level dyeings by the metachrome process, and the fastness to milling was sufficient to remove the trouble due to staining.

Mr. W. W. ENGLAND: What is the maximum pH value which a metachrome dyebath should be allowed to attain?

Mr. HANNAY: It is recommended that the pH of the dyebath should not be higher than pH 9. This is sufficiently high to produce satisfactorily level dyeings with any of the metachrome dyes, and avoids danger of damage to wool when there is also present in the dyebath a hydrolysable ester. It has been found that an initial pH of 8·7 is normally easily maintained if properly washed-off wool is used, and this initial pH is the one at which most of the work on the metachrome dyes has been done.

Mr. R. L. ROBINSON: We have obtained good results in the dyeing of loose wool, but our main concern as commission dyers has been the added cost of the ester technique.

Mr. HANNAY: Worthwhile advantages have been obtained. Thus very fast dyeings, particularly in pale shades, have been produced on loose wool with dyes which previously it had not been possible to use owing to the very unlevel results obtained by the normal techniques. A very good example is provided by carbonised wool stock dyed with a

mixture of Carbolan Crimson 3B and Alizarine Light Brown BL.

Mr. H. WHITWAM: In the dyeing of loose wool the cleanliness of the stock varies, and this has an effect on the final hue of the dyeings, particularly if dyeing is prolonged and pale shades are being dyed. It is customary in such cases to try to attain the final dyeings in as short a boiling time as possible. Does the use of esters enable the dyeing time to be cut down, and could good results be obtained in, say, 20 min. boiling?

Mr. HANNAY: It is difficult to give a very definite answer to this question. Most of the work done has been based on a boiling period of 45 min. as representing an average time, and excellent exhaustion with level results has been obtained in this time. With the neutral-dyeing acid dyes, there is a restraining action in the intitial stages of dyeing, and if the time is cut down too much poor exhaustion of the bath will result, although the dyeings will be level. My own opinion, based on observations of a number of dyeings, is that it would be unwise to cut the boiling time below 30 min. unless one is prepared to sacrifice a certain amount of dye owing to poor exhaustion. This in turn could lead to further difficulties if mixtures of dyes having differing initial strike and percentage exhaustion were being used, as the proportions of each dye would probably have to be modified in order to obtain the correct hue if the time were too short to allow the dyeing to reach normal completion.

COMMUNICATIONS

Some Aspects of the Drying and Heating of Textiles

VIII—Note on Modifications produced by Thermal Treatments of Acetate Rayon Fibres

J. M. PRESTON and M. V. NIMKAR

Modifications produced by heat and moisture in cellulose acetate fibres are described. These are similar to those described for other fibres in earlier papers. There is an optimum moisture content for the maximum modification on heating. The action of the moisture in the presence of heat indicates that it plasticises the substance of the fibres.

In an earlier paper [1] it was shown that thermal treatments decreased the subsequent swelling of viscose rayon, cuprammonium rayon, and silk fibres. In some later work, cellulose acetate rayon fibres have been examined in the same way. It is found that they exhibit analogous behaviour to that of the other fibres previously reported.

In addition to the reduction in swelling power brought about by the heat treatment, the acetate yarns heated under humid conditions showed adhesion between their filaments. This is in agreement with the plasticising effect of water on these fibres at high temperatures, which is used when stretching them [2].

Further evidence indicating the same behaviour is that moist cellulose acetate ironed at temperatures far below its melting point in the dry state appear to have been plasticised and partly fused together.

EXPERIMENTAL

The thermal treatments were carried out, as described previously [1], by heating the fibres in sealed containers with known moisture contents, at known temperatures, for one hour in every case. The water retention of each sample, after immersion followed by centrifuging at 1000 g for 5 min. [3,4], was measured. Furthermore, as it had been found previously that thermal treatments varied the contact angle, the contact angle of the untreated and treated fibres was measured by Adam's method [5]. This method is not of high accuracy, but for the purpose required gave significant results. The data for the moisture retentions for the temperature series at constant moisture content are

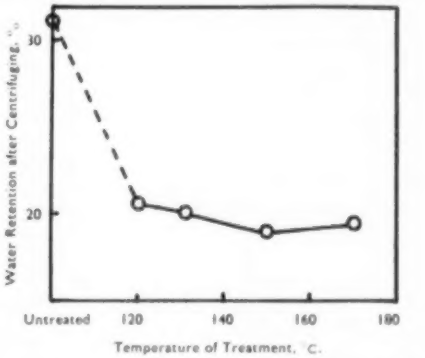


FIG. 1—Acetate Rayon with 15% Regain heated for 1 hr.

plotted in Fig. 1, and the data for the moisture series at constant temperature in Fig. 2. The data for receding contact angles are set out in Table I. All the treated fibres had a moisture content of 15% and were heated for 1 hr.

TABLE I

Temperature of Treatment (°C.)	Receding Contact Angle (°)
Untreated	30
120	45
132	45–50
150	50
170	50

It will be seen that thermal treatment reduces the water retention by as much as 10–12% compared with the untreated fibres.

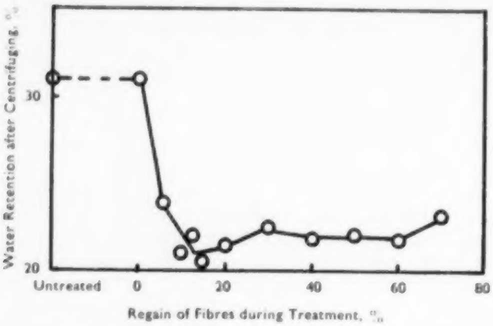


FIG. 2—Acetate Rayon heated at 120°c. for 1 hr.

The results of some experiments on the effect of ironing cellulose acetate fabrics under both dry and moist conditions are set out in Table II.

TABLE II

Temperature of Iron (°c.)	Fabric dry Glazed Appearance	Fabric dry Translucency	Fabric wet Glazed Appearance	Fabric wet Translucency
120	Slight	None	Marked	Slight
140	Slight	None	Marked	Distinct
175	Slight	None	Marked	Marked

DISCUSSION

It was shown in a previous paper [3] that the capillary water associated with fibres varies linearly with the cosine of the angle of contact. The amount of water retained by untreated acetate rayon fibres exposed to a centrifugal field of 1000 *g* for 5 min. can be obtained by subtracting the amount of water entering the fibres from the total water retained by the fibres. The amount of water entering the untreated fibres is known from other work [6] to be 19–20%; hence the capillary water present in these fibres is 12–13%. The reduction of this due to the change of contact angle from 30° to 50° can be calculated from the cosine law to be 2·5%. It is therefore clear that the reduced water retention shown in Fig. 1 and 2 for the treated fibres is caused by a change in the fibres themselves; i.e. the fibres show a reduced swelling after thermal treatments. These results for acetate rayon are in agreement with those found for the other fibres examined previously [1]. It will also be observed from Fig. 2 that there is a similar rapid fall in moisture retention with the initial increase of regain during heating. There is an indication of a minimum moisture retention at about 15% regain. This is about three-quarters of the value found for silk and about one-half of the value found for viscose rayon [1].

Although the regain at the minimum is at a lower value with acetate rayon than with silk and viscose rayon, it is a larger fraction of the saturation value.

It is significant that the handle of the fibres begins to be affected only at regains greater than that corresponding to the minimum in Fig. 2. This behaviour can be understood if it is considered that the fibres are plasticised at the temperature used, 120°c., and at the higher regains. It suggests that the lowering of the moisture retention is caused by a consolidation of fibre structure brought about in the less ordered regions of the fibres.

DEPARTMENT OF TEXTILE CHEMISTRY
COLLEGE OF TECHNOLOGY
THE UNIVERSITY
MANCHESTER

(*Received 5th December 1952*)

References

1 Preston, J. M., Nimkar, M. V., and Gundavda, S. P., J.S.D.C., **67**, 169 (1951).
2 Dreyfus, *BP* 557,004.
3 Preston, J. M., and Nimkar, M. V., *J. Textile Inst.*, **40**, P 674 (1949).
4 Preston, J. M., Nimkar, M. V., and Gundavda, S. P., *ibid.*, **42**, T 79 (1951).
5 Adam, N. K., J.S.D.C., **53**, 121 (1937).
6 Preston, J. M., International Congress on "Unity in the Textile Field" (Venice: Centro Internazionale delle Arti e del Costume, 1952).

A Simple Microthermostat for use in Colorimetric and other Optical Measurements

W. J. MARSHALL

A microthermostat has been constructed in an optical cell of side 6 cm. It has been used in making colorimetric measurements in the G.E. recording spectrophotometer and in other experiments employing optical techniques, but the method can equally well be applied to controlling the temperature of other small vessels such as beakers and flasks. The thermometric element is a small thermistor, and the temperature is controlled by the associated bridge circuit operating an electric heater of negligible thermal capacity.

In chemical reactions which are accompanied by a change in colour, the kinetics of the process can be followed very conveniently by observing the change in the absorption spectrum of the reactants with time. An example of this type which has been studied in these laboratories recently is the reduction of anthraquinone vat dyes [1]. In order to obtain a complete record of the process, it was thought desirable to carry out the reaction in an optical cell, so that measurements of the absorption spectra could be made continuously in the General Electric recording spectrophotometer. The reaction cell was in turn contained within a thermostat with sides of optical glass and of such small dimensions that it could be contained within the cell compartment of the spectrophotometer. This "microthermostat" has proved so successful and reliable in use and has aroused so much interest that a short account of its construction may be of interest to other workers in this field. The principles involved can, of course, be extended to the temperature control of other small vessels such as beakers and flasks.

The difficulties associated with control of temperature in a small vessel are largely due to the low heat capacity in relation to the large surface

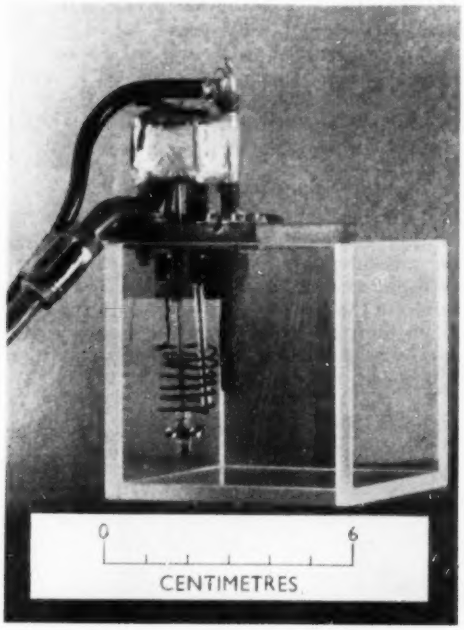
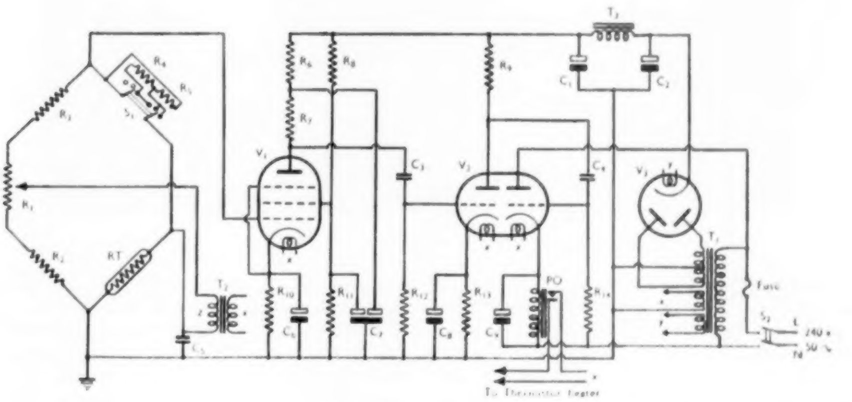


FIG. 1

area, which leads to a high rate of cooling. The accuracy of the control depends on the cooling during the period of time required by the control element to respond to changes of temperature and on the lag in the heat transfer from the heater to the bulk of the thermostat liquid. To avoid large fluctuations in temperature it is therefore necessary to employ a highly sensitive thermometric element, and both this and the heater must have a very low heat capacity. In the present instance these conditions have been fulfilled by the use of a thermistor of small dimensions as the temperature-sensitive element and a bare nichrome wire as the heater. The use of a thermistor has an additional advantage in that, since it is a resistance-type thermometer, the temperature can be preset from a calibrated dial in the associated bridge circuit, a valuable feature when a series of experiments at different temperatures are to be carried out. Efficient stirring is necessary to ensure that full advantage is taken of the rapid response of the thermistor and heater to give uniform temperature throughout the thermostat.

DETAILS OF CONSTRUCTION

The construction of the thermostat can be most easily seen from the photograph (Fig. 1). The tank is a 6-cm. cubical optical cell, the stirring motor, heater, and control element being fixed to a Tufnol



Resistances (ohms)

R_1	...	50,000 (potentiometer)
R_2–R_5	...	50,000 (wire-wound, Muirhead type A 60)
R_6–R_8	...	100,000
R_9	...	20,000
R_{10}	...	10,000
R_{11}	...	100,000
R_{12}	...	500,000
R_{13}	...	2,000
R_{14}	...	500,000
RT	...	Thermistor (Stantel type F 1512/300)

Capacitances (microfarads)

$C_1 + C_2$	...	16 + 16 (300 v. working electrolytic)
C_3, C_4	...	0·1 (non-inductive)
C_5	...	0·05–0·1 (chosen by trial)
C_6	...	25 (25 v. electrolytic)
C_7	...	16 + 16 (300 v. working electrolytic)
C_8, C_9	...	25 (25 v. working electrolytic)

Transformers and Chokes

T_1	...	Mains transformer (300–0–300 v.)
T_2	...	Inter-valve transformer (1 : 1·75)
T_3	...	Smoothing choke (30 H., 20 ma. D.C.)

Switches

S_1	...	Two-pole 3-way wafer
S_2	...	Two-pole toggle

Valves

V_1	...	6J7
V_2	...	6SN7
V_3	...	5Z4G
PO	...	G.P.O. relay type 2000 (2000 ohms)
x	...	6·3 v. A.C., 4 amp.
y	...	5 v. A.C., 2 amp.
z	...	10 v. A.C.

FIG. 2—Thermistor Relay Unit

mounting which covers half the cell. The 20-watt heater is a 2-ohm spiral of bare nichrome wire, the stirrer a small stainless-steel paddle driven by a miniature electric motor (Electrotor type 240), and the temperature-control element a Stantel thermistor type F 1512/300 [2]. This last is obscured in the photograph (Fig. 1) by the screening cable in which it is enclosed.

The most satisfactory method of using a thermistor for temperature control is to connect it in a Wheatstone-bridge circuit which is balanced when the thermistor is at the desired temperature. Any drop in temperature produces an out-of-balance current which operates the heater relay. Amplification is necessary, because the small size of the thermistor limits the amount of power which it may dissipate. Dickinson [3] has used a thermistor with D.C. amplification to control the temperature in a small air-oven, but the amplifier is difficult to stabilise; an A.C. bridge followed by a phase-sensitive relay forms a robust and stable unit which is more suitable for continuous laboratory use. The circuit in Fig. 2 has been found to give excellent results and requires little attention for long periods.

The principle of operation is as follows— The off-balance voltage from the bridge, which is supplied with 10 v. A.C. through a small transformer, is amplified in the normal way. The amplified signal, whose phase depends on whether the temperature is too high or too low, controls the current through the second half of V_2, increasing or decreasing it according to whether the signal is in phase or in anti-phase respectively with the anode supply. Thus the relay *PO* responds only to a fall in temperature. The condenser C_5 is required to balance out inter-winding capacities in the transformer T_2.

No particular precautions are necessary for the circuit layout apart from the desirability of keeping unscreened leads short. The thermistor leads are screened, and the thermistor itself is enclosed in the end portion of the screening. The heater current and the current for the stirring motor are carried in a cable which is taped to the thermistor leads, so that only one set of leads is required between the thermostat and the control unit. No interference due to the proximity of these wires has been observed.

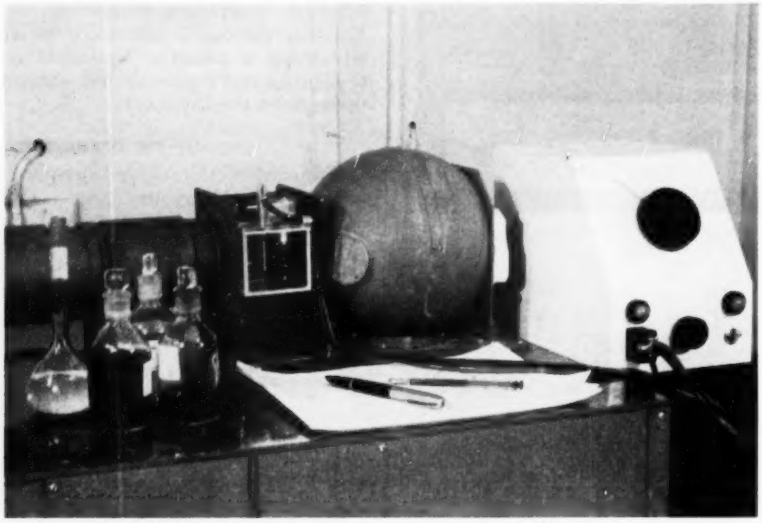


FIG. 3

THE MICROTHERMOSTAT IN USE

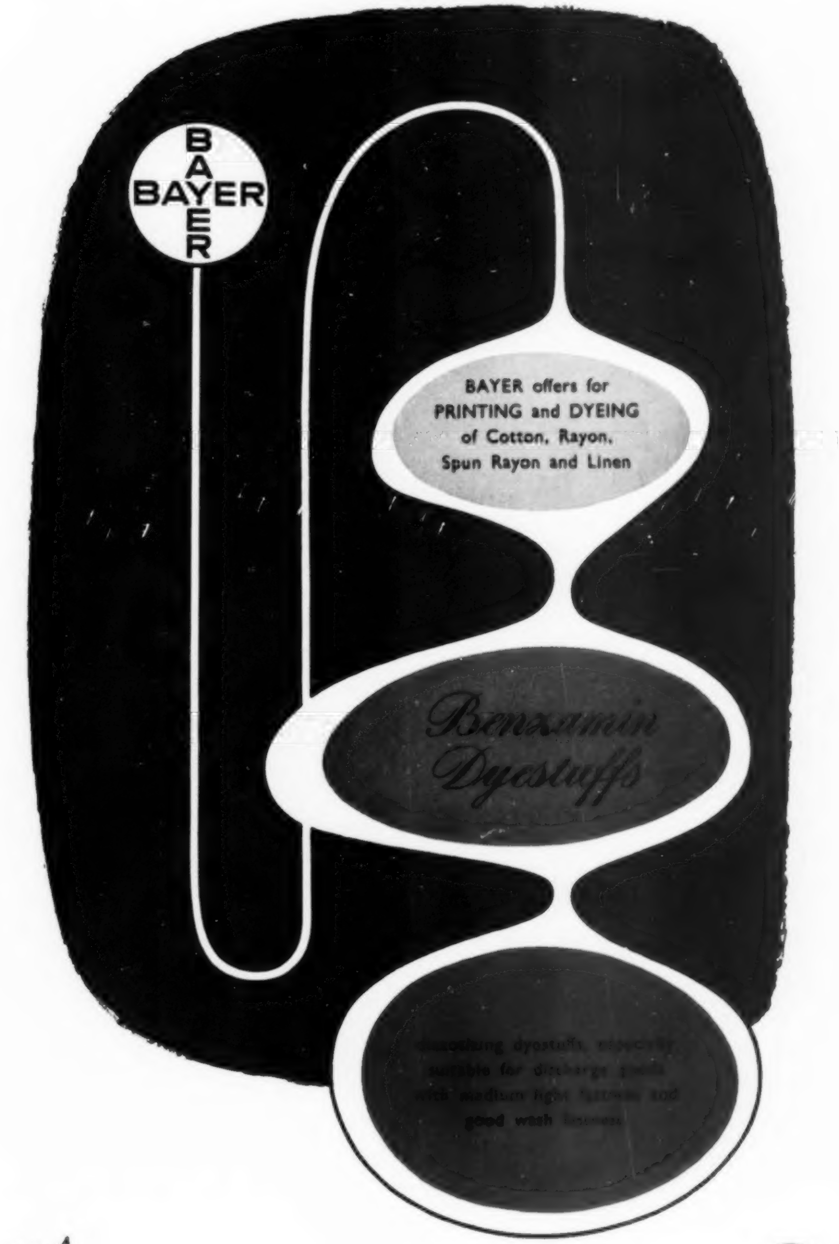
As already mentioned, the apparatus was primarily constructed for carrying out reaction rate measurements with the G.E. recording spectrophotometer. Fig. 3 shows the thermostat in position in the spectrophotometer with the control unit on the right-hand side. The accuracy of the control varies with the temperature and is proportional to the heat losses, but in day-to-day usage with a room temperature of about 20°c. it has been found that the temperature control is ±0·02°c. at 30°c. and ±0·05°c. at 40°c. Up to this temperature the thermostat liquid was water, but above this ethylene glycol was used to avoid trouble from water vapour entering the optics of the spectrophotometer. The higher viscosity of ethylene glycol reduces the efficiency of the stirring, and at 60°c. the temperature varied by as much as 0·3°c. and small differences of temperature were noted between the side and the centre of the thermostat. These figures do indicate, however, that even in such a small cell as this temperature control far beyond expectations, and satisfactory for many purposes, can be achieved.

DYEHOUSE LABORATORIES
IMPERIAL CHEMICAL INDUSTRIES LTD.
HEXAGON HOUSE
MANCHESTER 9

(*Received 29th December 1952*)

References

[1] Marshall and Peters, J.S.D.C., **68**, 289 (Aug. 1952).
[2] *Stantel Thermistors* (Standard Telephones & Cables Ltd.).
[3] Dickinson, *Electronic Engineering*, **21**, 408 (1949).


BAYER
BAYER offers for
PRINTING and DYEING
of Cotton, Rayon,
Spun Rayon and Linen
Benzamin
Dyestuffs
FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT
LEVERKUSEN
BAYER

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Disperse Dyes

When I read the prospectus for the Second Edition of the *Colour Index*, which will be published at the earliest in 1955, the following point occurred to me. The so called "acetate dyes" appear to be the first choice for the new synthetic fibres, all distinguished by low water imbibition. Before the new *Colour Index* is published, the output of the nylon, Terylene, Dacron, Orlon, and dynel groups of synthetics may eventually equal or surpass that of acetate rayon. The Second Edition of the *Colour Index* with American partnership will be the international authority on dyes. Is it not undesirable to particularise a group of dyes by the name of one fibre, when it has proved suitable for so many of the newer synthetic fibres? May I suggest that a new name for this group of dyes should be promoted in an international index?

In view of the definition of disperse dyes recommended by the Society's Terms and Definitions Committee [1], the term *disperse dyes* appears to be the most appropriate for this group of dyes.

C. M. WHITTAKER

1 WEAPONNESS PARK
SCARBOROUGH

17th May 1953

[1] J.S.D.C., **69**, 121 (April 1953).

Notes

Proceedings of the Council

At a meeting of the Council held at the offices of the Society, 19 Piccadilly, Bradford, on 13th May 1953, the proceedings included the following items of interest—

PUBLICATIONS COMMITTEE—The resignations of Dr. P. W. Cunliffe, Dr. H. H. Hodgson, and Mr. J. M. Preston were accepted, and it was resolved that they be thanked for their past services. It was decided to invite Mr. H. C. Olpin and Dr. A. E. Stubbs to serve on the committee.

MEMBERSHIP OF COMMITTEES OF THE SOCIETY—The membership of committees was further reviewed. The following resignations were accepted with regret—Mr. F. Scholefield from the Mercer Lecture Committee, Dr. H. H. Hodgson and Mr. W. P. Walker from the Historical Records Committee, and Dr. P. W. Cunliffe from the Dyeing Affinity of Regenerated Cellulose Committee. It was reported that the following invitations to serve had been accepted—Mr. H. H. Bowen on the Diploma Committee, Mr. J. G. Evans on the Worshipful Company of Dyers Research Medal Committee, Mr. D. B. F. McAndrew on the Society's Medals Committee, and Mr. A. J. Crockatt on the Perkin Centenary Committee.

REPRESENTATION ON EXTERNAL BODIES—The resignations were accepted of Mr. E. G. Harris from the Silk Industry Standards Committee of the British Standards Institution, of Mr. F. L. Goodall from Technical Committee D of the Textile Institute, and of Mr. A. Thomson from the County Advisory Committee for Textiles of the Yorkshire Council for Further Education. The following were nominated to represent the Society—the Chairman of the Terms and Definitions Committee (Dr. T. Vickerstaff) on the B.S.I. Colour Terminology Committee, Mr. W. Armfield on the T. I. Technical Committee D, and Mr. G. E. Styan on the Yorkshire Advisory Committee for Textiles.

NEW *EX-OFFICIO* MEMBERS OF COUNCIL—It was reported that Mr. S. R. Meadows and Mr. G. S. J. White had recently been elected Chairman of the Midlands Section and Chairman of the Manchester Section respectively.

MEMBERSHIP—Fourteen applications for ordinary membership and one application for junior membership were approved.

Meetings of Council and Committees May

Council—13th
Finance—13th
Publications—19th
Textile Printing Symposium—22nd
Colour Index Editorial Panel—6th
Diploma—5th
Fastness Tests Co-ordinating—6th
Joint Standing Committee with the Textile Institute—11th

Deaths

We regret to report the loss by death of Mr. G. E. Holden, C.B.E. (President of the Society 1948–1950), Mr. J. Prunell, and Mr. J. H. Smith.

Annual Dinner 1954

Arrangements have been made to hold the Seventieth Annual General Meeting and Dinner of the Society at the Midland Hotel, Manchester, on Friday, 30th April 1954.

Joint Conference with the Textile Institute Whitsun 1954

The Councils of the Society and of the Textile Institute have approved a recommendation of the Joint Standing Committee that the two bodies should jointly organise a conference on "Some Aspect of Colour in relation to Textiles", to be held at Scarborough during Whitsun week 1954 (June 8–11th).

Annual Meeting of Section Officers

The annual meeting of Chairmen and Honorary Secretaries of Sections was held at the May Fair Hotel, London W.C.1, on Saturday, 11th April 1953, under the chairmanship of Mr. H. Jennison (Honorary Treasurer of the Society). Among the chief topics of discussion were membership and subjects for lectures in the 1953–1954 session.

Terms and Definitions
Liaison with the Textile Institute

In order to avoid overlapping in work on terms and definitions, Council has nominated, in response to an invitation from the Textile Institute, the Chairman and the Honorary Secretary of the Terms and Definitions Committee (Dr. T. Vickerstaff and Mr. H. C. Olpin respectively) to represent the Society on the Textile Terms and Definitions Committee of the Institute. Similarly, the Institute will be represented on the Society's Committee by Mr. G. Loasby (Chairman of the Institute's Committee) and Dr. B. P. Ridge.

Willstätter Memorial Lecture
Richard Willstätter 1872–1942

Sir Robert Robinson has given in the Willstätter Memorial Lecture (*J.C.S.*, 999–1026 (March 1953)) a comprehensive survey of the life and work of Richard Willstätter, one of the greatest pioneers of Organic Chemistry. He followed Baeyer as Professor at Munich in 1915, resigning in 1925 but continuing research until 1939, after which he lived at Muralto-Locarno in Switzerland until his death on 3rd August 1942. At Zürich (1905–1912) he had carried out investigations on quinones and quinoneimines, which included the discovery of *o*-benzoquinone and 2:6-naphthaquinone, a vital contribution to the chemistry of aniline black, and an intensive programme of work on chlorophyll with the discovery of magnesium as a constituent, the correlation of the leaf and blood pigments, and the proof that leaf carotene is identical with the substance from carrots and that its isomer lycopene is the colouring matter of the tomato. For the next few years the chemistry of the red, purple, and blue colouring matters of flowers, fruits, and leaves occupied his attention, his first paper on the anthocyanins in general, and the cornflower pigment in particular, establishing the main lines of his subsequent investigations. In addition to the themes mentioned, the catholicity of Willstätter's interests emerges from a long list of chemical topics, including ornithine and other amino acids, the theory of dyeing, pyrones, reduction of lignin and carbohydrates with hydriodic acid and phosphorus, alkalimetric estimation of amino acids and peptides, vinylacetylene, hydrolysis of cellulose, indigoids from halogenated naphthols (of interest in colour photography), the rearrangement of naphthaquinone phenylhydrazones, the constitution of purpurogallin, and the blue colour of sea water, which he thought might be due to copper-ammines. His work with Zechmeister on cellulose in 1913 has been made the basis of a technical process, and E. Berl (1942) has remarked that the so called "Bergius process" for the saccharification of wood should be called the *Willstätter process*.

H H H

Association Internationale de la Teinture Textile

A meeting of the A.I.T.T. in Paris on 6th December 1952, attended by representatives from Austria, Belgium, France, Germany, Italy, and Switzerland, considered the removal of import duties and export subsidies from dyes, and also an Italian suggestion of an international mark for fast dyeings. Other topics discussed included professional education, effluents, and comparisons of costs.

Research Fellowships at Government Scientific Establishments

A small number of research fellowships, tenable for three years, are being instituted at Government scientific establishments, and will be advertised by the Civil Service Commission as the occasion arises. A considerable choice of subject will be allowed to research fellows.

Safe Handling of Cresols

In industry cresols are a hazard mainly to the eyes and the skin, although they are also toxic and represent a moderate fire risk. A recent member[1] of a series of chemical safety data sheets prescribes safe methods of unloading, emptying, handling, storing, and disposing of these compounds, and also describes health risks and their control.

[1] Manual Sheet SD–48, available from the Manufacturing Chemists' Assocn. Inc., 246 Woodward Building, Washington 5, D.C.— Price, 25 cents (prepaid).

British-made Phloroglucinol

Permission has been granted for the erection of an explosives store near the centre of Loughborough, to hold not more than 600 lb. of trinitrotoluene (T.N.T.). This is required for the manufacture of phloroglucinol, previously imported from the U.S.A.

Swiss Exports of Dyes

Swiss exports of dyes decreased in value from Swiss fr. 276·4 millions in 1951 to Swiss fr. 179·5 millions in 1952. The corresponding figure for 1938 was 83·0.

Tovis and Acetovis—Japanese Crimped Viscose Staple and Acetylated Viscose Staple

Tovis is a crimped viscose staple fibre made by the Toho Rayon Co. Ltd., Japan. Acetovis is an acetylated fibre made by treating Tovis with acetic anhydride vapour until approx. 50% acetylation is obtained.

C O C

Spontaneous Combustion of Wool Cargos

Research carried out in New Zealand[1] indicates that the fires are confined to wools removed from skins by a bacterial process. Such wools often contain a high percentage of body fat, which can be removed only by very thorough scouring.

[1] New Zealand, *Twenty-sixth Annual Report of the Department of Scientific and Industrial Research* (Wellington: Government Printer, 1952. Pp. 84. 1s 9d.).

Film on Sampling Technique

A film entitled *The Technique of Sampling* (16 mm. black and white, 30 min.) has been made by ICI expressly for analytical chemists, and includes some of the methods used for coal, penicillin, cotton (for leathercloth), and ammonia.

Tetrachloroethylene in Dry Cleaning

According to Shepherd[1] tetrachloroethylene is gradually replacing trichloroethylene for garment cleaning, because of the tendency of the latter to bleed acetate rayon dyes at temperatures above 80°F.

[1] Shepherd, C.B., *Chem. Eng. News*, **31**, 235 (19 Jan. 1953).

Colour of Demerara Sugar

In a report presented to the Food Standards Committee of the Ministry of Food by its Metallic Contamination Subcommittee it is stated that addition of tin chloride during manufacture to stabilise the colour has been largely replaced by the use of titanous chloride or an artificial colouring matter.

OBITUARY NOTICE

Harold Barnes

We regret to report the death on 20th October 1952, at the age of 59, of Mr. H. Barnes, who had been a well known figure in the dyeing trade for many years. Mr. Barnes entered the service of J. & J. Baldwin & Partners Ltd. in 1908 as an apprentice dyer, and spent the whole of his working life with that firm and their successors, Patons & Baldwins Ltd. For over thirty years he was Dyehouse Manager at the Halifax factory, with short intervals at the Melton Mowbray and Alloa mills. In 1949 he removed to Darlington to take charge of the large modern yarn dyehouse in the new factory there.

Mr. Barnes will be remembered by a great number of friends not only for his interest in the application of dyes but also for his work in musical circles. In his younger days he had a fine baritone voice and took many leading parts in the productions of the Halifax Light Opera Society. Later he became conductor of that society and was responsible for a number of productions. During the war he gave his services freely in organising concerts for members of the Armed Forces stationed in the West Riding and travelled thousands of miles to provide some 300 concerts, many of them in remote villages. He will also be remembered by members of the West Riding Section for the excellent entertainment he provided at several of the smoking concerts given by that Section.

Mr. Barnes is survived by a widow, a son, and two daughters.

H. V. Dyson
J. F. Gaunt

New Books and Publications

Modern Textile Auxiliaries

Edited by A. J. Hall. Pp. xii + 200. Manchester: Thomas Skinner & Co. Publishers Ltd. 1952. Price, 21s. 0d.

Textile processors now have at their disposal a very wide range of chemical substances which can be employed to assist in manufacturing operations and to produce valuable effects either in dyeing or in finishing. To have information about these products gathered together in one volume is therefore of considerable value to all concerned with the technical aspects of textiles. Mr. Hall has done a service by indexing a large number of these products, and providing notes on their properties and uses.

His book is well printed, and arranged in four parts for easy reference. Following his introduction, there is a main section giving collected information, next follows an alphabetical index, and finally a classified list of applications. The main section is not arranged according to any clearly defined plan, but this defect is made good by the alphabetical index.

In his introduction Mr. Hall makes the interesting point that wholly synthetic auxiliary products are now of great importance, and that dependence on products derived from animal or vegetable sources is decreasing. He also comments on the discovery of the valuable technical applications of organosilicon compounds. In this connection it is rather regrettable that he adds to the debt owed to the late Professor F. S. Kipping of Nottingham University College for discovering these substances by ascribing them to Professor Perkin.

In a compilation of this kind there are almost inevitably some mistakes; e.g. the structural formula given on p. 150 for Ammonyx T is clearly incorrect. One wonders, too, whether the inclusion of litmus on p. 144 is really necessary to the completeness of the book. P. T. Gale

Encyclopedia of Surface-active Agents

By J. P. Sisley, translated and revised by P. J. Wood. Pp. iv + 540. New York: Chemical Publishing Co. Inc. 1952. Price, $15.00.

The Textile Industries have always provided a powerful stimulus to the manufacture of new organic chemicals, and an important development in the past thirty years has been the increasing production of substances used to facilitate textile manufacture and processing. Many of these products are simple wetting agents, detergents, and emulsifying agents, but others are very specific in their action and have enabled methods of dyeing and finishing to be devised which otherwise would have been impracticable.

Since all that is required in the simpler surface-active agents is a long fatty chain with a solubilising group attached somewhere along its length, it is not surprising that many products have been put on the market which can be used interchangeably in the day-to-day operations of textile wet processing, as well as in many other industrial applications.

Monsieur Sisley has set himself the task of classifying and describing the large number of surface-active agents which have appeared over the years, and has arranged them in broad groups according to chemical type. In addition he has provided an index, evidently compiled from manufacturers' literature, giving notes on constitution, properties, and uses. This is possibly the most useful section of the book.

The book is a translation from the French by Mr. P. J. Wood, and the English is not always clear and unambiguous. The text also contains a number of obvious errors: e.g. on p. 100 it is stated that *cetyl* bromide heated with pyridine gives *octadecyl*pyridinium, and on the same page a reaction for the preparation of dodecylpyridinium sulphate is given which seems very improbable. In the index Trilon B is incorrectly described, and the constitution assigned to it is that of Trilon A.

The book would have been improved by a more critical approach, and where named products are no longer commercially available notes should be included to that effect. P. T. Gale

Statistical Methods for Chemical Experimentation

By W. L. Gore. Pp. xi + 210. New York and London: Interscience Publishers, 1952. Price, $3.50 (25s. 0d.).

The value of statistical methods in chemical research and development is now firmly established by useful applications in numerous fields of work, and the only real hindrance to a still wider application of these methods is the difficulty of training the chemist in the use of them. Any book that will help him is therefore very welcome; and although there may (and in fact there do) already exist quite a large number of general textbooks, the chemist will naturally prefer one that is written more specifically for his own particular requirements, so long as it also satisfies the general requirements of being a sound and clear exposition. As its title indicates, the present work is intended as a handbook for the chemical experimenter.

The opening chapter comprises a summary description of the purpose and scope of statistical methods, and this is followed in Chapter II by the elementary basic material concerning frequency distributions and measures of location and dispersion. These ideas are then developed in Chapter III, leading to the simpler tests of statistical significance; and the more general method of analysis of variance is described in Chapter IV. The main feature, design of experiments, is dealt with fairly extensively in Chapter V (which takes up nearly one-third of the whole book). This is followed by a chapter on correlation and regression, and one on the analysis of frequency counts. Finally there are appendixes of statistical tables and formulæ, a glossary, and a short bibliography.

The subject-matter that the author has attempted to expound certainly includes a useful range of techniques which are likely to help the chemist in his work; but the book cannot be recommended as giving a clear account from which the average reader will, without undue difficulty, be able to obtain an adequate understanding of the methods and of the way in which they should be applied. The book suffers to a very large extent from sheer clumsiness of expression and careless presentation, with the result that the reader will not only find it difficult to obtain any clear understanding of the subject but is also likely in certain cases to be seriously misled. The author does, indeed, make many useful points, some of them in quite cogent fashion; but these merits are almost completely outweighed by the above faults.

The chemist, who in any event has little time to spare for such ancillary studies, deserves something much better than this. It is admittedly no easy task to write an account of statistical methods that is practical, non-mathematical, logically convincing, and yet short enough to appeal to the busy worker: it requires a combination of very clear thinking, good writing, careful choice and presentation of material, and systematic development. The pen of the author has not risen to the occasion. D. R. Read

Mothproofing from the Entomological Point of View

(*Mededeling van het Vezelinstituut T.N.O. No. 109*)

By A. D. J. Meeuse. Pp. iii + 53. Delft: Vezelinstituut T.N.O. [1951.] Price, florins 6.00.

This book is written in a very interesting way and contains a valuable bibliography. The writer is a biologist and this side is, perhaps, emphasised, though it is of interest to note that he states: "the best place to carry out applied research on mothproofing is a textile laboratory with a biological section, where the entomologist and the textile chemist can co-operate, the more so because the majority of the practical problems and questions relating to this subject emanate from textile mills and dry-cleaning establishments and these industries are already in contact with textile research laboratories for other reasons."

There is a good survey, with some excellent plates, of the insects responsible for damage to keratin and of the methods for rearing the various insects under laboratory conditions.

Methods of test for various materials are described in detail, and there is a useful discussion on the methods used on the Continent, in the U.S.A., and in Great Britain.

Attention is drawn to the possibility of error if reliance is placed solely on chemical estimation of the amount of a proofing agent present, and emphasis is laid on the biological test.

J. Barritt

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

Resistance of various Materials to Corrosion in Sodium Chlorite Solutions—III. J. Meybeck and N. Iwanow. *Bull. Inst. Text. France*, (36), 7–25 (Dec. 1952).

Test pieces were immersed at 80°C. in aq. soln. of $NaClO_2$ (5 g./litre) acidified with acetic acid to pH 4. Pb, Ni, Zn, Cu, ordinary Al, and Al alloys were badly corroded, while a 55% Cu + 45% Ni alloy and Al of 99·99% purity were only slightly attacked. The rate of decomposition of the chlorite soln. is also specific to the metallic nature of the specimen; it was highest when rapid corrosion occurred. 12 plates. G. L.

PATENTS

Continuous Spinning of Viscose Rayon. American Viscose Corpn. *BP* 688,493

A roller-type machine for the continuous spinning of viscose rayon is described. W. G. C.

Continuous Spinning of Viscose Rayon. Vereinigte Glanzstoff-Fabriken. *BP* 688,524

In the continuous spinning of viscose rayon by the roller type of machine, the thick liquid sheath round the ascending thread can be avoided by having the lower roll of such a shape that the thread carries off 25–33% of the quantity of treating liquid which it carried with it as it ran on to the lower roll. Longitudinal fluting having a triangular profile is suitable for the purpose. W. G. C.

Apparatus for Treating a Continuously Moving Thread with Liquid. American Cyanamid Co. *BP* 689,770

Continuously moving thread is passed through liquid in a vessel having bottom, side, and end portions, each end portion having an opening or slot through which the thread passes, and the vessel containing also a troughlike member which is parallel to the sides of the vessel and through which the thread passes. The trough is open-ended and contains a series of spaced apertures extending from one end to the other, through which treatment liquid is passed so that it flows over the filament as the latter moves along the trough, waste liquor passing over the ends of the trough and into the vessel, whence it is drained away. J. W. B.

Klauder-Weldon Dyeing Machine having Improved Sticks and Mountings therefor. G. V. Greaves. *USP* 2,611,258

Mountings for Rollers. Crosland & Pickstone. *BP* 689,247

In machines for processing cloth in which the cloth passes over rotatably mounted members, the freedom of the cloth to shrink is not restricted by passing over such members if they are each mounted at each of their ends on a short shaft or axle carried in bearings supported by the frame of the machine. One of each pair of axles rotates in one direction and the other in the opposite direction, their speeds being equal and greater than that imparted to the member by the cloth passing over it. This overcomes the static friction at the bearings, so that the member "floats" and assumes the speed of the cloth passing over it, and so places a minimum of restraint to dimensional change in the cloth. C. O. C.

Impregnating Fibres, etc. Alexander H. Kerr & Co. *USP* 2,611,336

A machine suitable for impregnating fabrics, particularly glass fabrics. C. O. C.

Calender. T. Merchant. *BP* 689,197

The cloth passes between a pair of metal rollers placed in front of the calender rollers. These rollers cause any metal particle in the cloth to cut a single hole in it and drop out before the cloth reaches the calender rollers. C. O. C.

Embossing Calender. Champion Paper & Fibre Co. *USP* 2,611,312

Machine for embossing paper on both sides in a single passage. The relative intensities of the impressions on opposite sides of the paper can be readily adjusted. C. O. C.

Straightening Bowed Weft Threads in Fabrics. J. D. Robertson. *BP* 689,177

Apparatus is described in which several longitudinally curved rollers are mounted in clamps which are adjustable either manually or automatically in response to electrical scanning means. C. O. C.

Printing Screens. A. C. Chuzel. *USP* 2,608,750

Machine for affixing the gauze in making printing screens. C. O. C.

Screen Printing of Hosiery. May Hosiery Mills. *USP* 2,609,747

Dry Cleaning Apparatus. J. P. Spencer. *BP* 689,185

An improved outlet for extracted liquors which prevents their being circulated round and round the casing or being thrown out of the air inlet and/or outlet. C. O. C.

Laundry Ironing Machines. Baker Perkins. *BP* 689,639

Garment Presses. Grimsley & Co. Leicester. *BP* 690,633

On the press being closed steam and then suction are automatically applied to the garment. C. O. C.

Steaming and Pressing of Clothing. Kleindienst & Co. Maschinenfabrik und Eisengiesserei. *BP* 690,455

The garment is steamed from inside while on a lay figure or bust, and at the same time is given a fashioning treatment similar to that obtained by pressing. C. O. C.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Xanthation of Cellulose. I—Reaction of Carbon Disulphide with Caustic Soda. P. M. Cherkasskaya, A. B. Pakshver, and V. A. Kargin. *J. Appl. Chem. U.S.S.R.*, **26**, 63–69 (Jan. 1953).

When CS_2 is treated with NaOH, two successive reactions occur—

$$6NaOH + CS_2 = 2Na_2S + Na_2CO_3 + 3H_2O$$

$$Na_2S + CS_2 = Na_2CS_3$$

Rate constants and activation energies relating to these reactions are determined. A. E. S.

Foaming of Surface-active Agents. F. Kroemer and G. Ehrhard. *Melliand Textilber.*, **34**, 127–129 (Feb. 1953).

The influence of hardness, pH, and addition of phosphate on the foaming properties of a variety of commercial surface-active agents is investigated. Almost always increased hardness considerably reduces foaming, but decreased pH has little effect. The action of phosphate depends on the type of phosphate, its concn., and the nature of the surface-active agent—several optima are noted. H. E. N.

Special Reactivity of the Two End-groups of Long Chains. R. Senzyu and O. Asayama. *Bull. Chem. Soc. Japan*, **25**, 312–314 (Oct. 1952).

The rates of saponification of β-methoxyethyl acetate and polyethylene glycol diacetate in 0·1 N-NaOH are measured at 10° and 25°C. Reaction constants, activation energies, and entropies of activation are calculated and are identical for both compounds. A. J.

Reactions of Vinyltrichlorosilane and Vinyltriethoxysilane. G. H. Wagner, D. L. Bailey, A. N. Pines, M. L. Dunham, and D. B. McIntire. *Ind. Eng. Chem.*, **45**, 367–374 (Feb. 1953).

A study of the reactivity of the vinyl group attached to silicon has shown that it can undergo halogenation, hydrohalogenation, the Friedel-Crafts reaction, the Diels-Alder reaction, and polymerisation. Under certain conditions of hydrolysis, vinyltrichlorosilane gives soluble siloxanes which appear to be chains of *cyclo*-tetrasiloxanes. There are differences in the reactivity of the vinyl groups in vinyltrichlorosilane, vinyltriethoxysilane, and vinylpolysiloxane. Other silicon monomers, e.g. *cyclo*hexenyltrichlorosilane, β-phenylethyltrichlorosilane, etc., may be prepared from vinyltrichlorosilane. W. K. R.

PATENTS

Surface-active Alkylbenzenesulphonate Compositions. Monsanto. *BP* 690,288

A mixture of 55–70% by wt. of a sodium alkylbenzenesulphonate (Alk on average of 9 C) with 45–30% of another sodium alkylbenzenesulphonate (Alk on average of 12 C) yields 30% aqueous solutions which remain clear at low temperatures. C. O. C.

Detergent. California Research Corpn. *USP* 2,610,950

A mixture of alkali-metal sulphate (23–41%), normal alkali-metal pyrophosphate (14–44), fatty-acid soap (6–25%), and alkali-metal alkarylsulphonate (15–28) has high detergency combined with high foam-forming ability. C. O. C.

Detergent. Polysulphin Co. *BP* 689,171

A detergent which deposits more readily in the material to be washed, and remains longer in contact with it, than previously known detergents comprises a homogeneous solution in an anhydrous soap-forming fatty acid of an anhydrous salt which is an anionic surface-active agent. The composition is such that its aqueous dispersion at pH 5–7 appears homogeneous. C. O. C.

Detergents. Procter & Gamble Co. *BP* 689,246

The products obtained by sulphonating compounds of formula $R{\cdot}CO{\cdot}X^1{\cdot}C_nH_{2n}{\cdot}CO{\cdot}X^2{\cdot}Y$ (R·CO = acyl groups of either sat. fatty acids of 8–22 C or mixed fatty acids of 8–22 C the I.V. of the equivalents being $\not> 20$; $n = 1$–3; X^1 and X^2 = O or NZ; Z = H or Alk of < 4 C; Y = alkenyl of 3 or 4 C) are detergents which are unaffected by hard or salt water or by dil. acid or alkali. C. O. C.

Guanidine Alkarylsulphonates—Detergents. Lever Brothers & Unilever. *BP* 690,439

Compounds of formula $Alk{\cdot}Ar{\cdot}SO_3(NH_3{\cdot}C(NH_2){:}NH$ (Alk of 6–18 C; Ar = subst. or unsubst. phenylene) are non-hygroscopic detergents. C. O. C.

Polyglycol Ethers of 3:5:5-Trimethyl-1-hexanol. Monsanto. *BP* 690,564

Compounds of formula—

$$CH_3{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}[C_2H_4{\cdot}O]_x{\cdot}H$$

(x = 1–20) are wetting agents, detergents, and plasticisers. C. O. C.

Polyglycol Ethers—Warp-sizing Agents. FBy. *BP* 690,355

Waxlike polyglycol ethers are obtained by treating a polyhydric alcohol containing $>$ 2 OH groups with $>$ 20 mol. of an alkylene oxide for each OH. They are readily soluble in cold water and are suitable for sizing warps. C. O. C.

Substituted Sulphonamides—Auxiliary Agents. Henkel & Cie. *BP* 690,423

The products obtained by treating an alkylbenzenesulphonyl chloride with an aromatic aminosulphonic acid, preferably sulphanilic acid, are oily to solid and more or less soluble in water. They may be used as wetting and softening agents, detergents, etc. C. O. C.

Stable Water-soluble Urea-Aldehyde Condensates. Deutsche Gold- und Silber-Scheideanstalt. *BP* 689,327

The condensates obtained by treating 1 mol. of urea and/or thiourea in acid aqueous medium with 0·25–1·0 mol. of acrolein and then under alkaline conditions with 1·25–3·75 mol. of H·CHO, the total amount of aldehydes used being 1·5–4·0 mol., form clear solutions which are miscible with water in all proportions and limitlessly stable. They are used as textile finishes, etc. C. O. C.

Water-repellent Agents. Dow Chemical Co. *USP* 2,608,495

Compounds of formula $R^1_nSi(O{\cdot}CO{\cdot}R^2)_{4-n}$ (R^1 in each case = hydrocarbon or hydrocarbon-oxy, at least one R^1 being Alk or Alk·O of $>$ 7 C; R^2 = hydrocarbon; n = 1–3) are waterproofing agents for textiles. C. O. C.

Flameproofing Composition. H. Hopkinson. *USP* 2,610,920

A mixture of a metallic oxide (40–65% on the weight of the mixture), an inhibitor which retards liberation of HCl, e.g. basic lead carbonate, calcium or lead silicate, or lead sulphate (20–40% on the wt. of metallic oxide), a glowproofer, e.g. octadecylamine phosphate, borate, or silicate (10% on the wt. of the mixture), and a metallic salt of a weak inorganic acid, e.g. titanium stannate or magnesium zincate (10–25% on the wt. of the mixture) is either ground with a chlorinated plasticiser, e.g. methyl pentachlorostearate, and/or is mixed with a chlorinated film-former, e.g. chlorinated rubber or polyvinyl chloride, in the application bath. The flameproof given by such a composition resists weathering or repeated laundering. C. O. C.

Carboxymethyl Cellulose (XI p. 225).

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Japanese Dyemakers' Difficulties. Anon. *Dyer*, **109**, 469–474 (3 April 1953).

A survey of the Japanese dyemaking industry from its inception in 1914. Cycles of expansion and recession are discussed, and tables are given which set out production and export figures for various dye classes. It is stated that there is now a movement towards the production of high-grade dyes, most of which have hitherto been imported. A. H.

Separation of 1- and 2-Methylnaphthalenes by Azeotropic Distillation. J. Feldman and M. Orchin. *Ind. Eng. Chem.*, **44**, 2909–2914 (Dec. 1952).

Mixtures of the isomers were distilled with excess undecanol at 260 mm. pressure. When all the 2-methylnaphthalene had been removed, the undecanol was distilled off at atmospheric pressure. The residue was distilled, and yielded 99·2% pure 1-methylnaphthalene. B. M.

Synthesis and Physical Properties of Alkylnaphthalenes. D. G. Anderson, J. C. Smith, and R. J. Rallings. *J.C.S.*, 443–450 (Feb. 1953).

Earlier syntheses have been extended up to 1- and 2-*n*-hexadecylnaphthalene, and a generalisation is given on the methods of preparation suitable for each series. For the α-substituted naphthalenes the size of the alkyl chain determines which method is most appropriate: e.g. 1-methylnaphthalene is obtained pure from the commercial (60%) product by the sulphonation–desulphonation process (Coulson, *J.S.C.I.*, **62**, 177 (1943)); 1-ethyl- and 1-propyl-naphthalene are prepared through the ketones; and from 1-heptyl- to 1-hexadecyl-naphthalene, the condensation between 1-naphthylmagnesium bromide and the alkyl cyanide gives good results. For the β-compounds the Friedel–Crafts reaction between an acid chloride and naphthalene (or tetrahydronaphthalene) in nitrobenzene is always used, as the β-ketone is then readily obtained pure and in high yield. A summary of the physical properties of 1- and 2-alkylnaphthalenes is given, and the changes from aromatic to aliphatic characteristics are shown. H. H. H.

Hydrates of Naphthalene-β-sulphonic Acid. J. S. F. Gill and M. J. Thornton. *J.C.S.*, 914–921 (March 1953).

The complete phase data for the system naphthalene-β-sulphonic acid–water are presented. Four hydrates—mono, tri, penta, and octa—of the β-acid exist; only the first two have previously been described. An exact thermodynamic relationship has been applied to the pressure–temperature curves. H. H. H.

Methyl β-Naphthyl Sulphide. Ng. Ph. Buu-Hoï, Ng. Hoán, and D. Lavit. *J.C.S.*, 485–489 (Feb. 1953).

Methyl β-naphthyl sulphide is shown to undergo reactions similar to those of its oxygen analogue, e.g. formylation, Friedel–Crafts reaction, etc.), but less readily. Nine α-substituted β-(6-methylthio-2-naphthyl)acrylonitriles, fourteen substituted 2-(6-methylthio-2-naphthyl)-quinolines, seventeen 2-substituted 7-methylthio-1-azaphenanthrene-4-carboxylic acids, and eight 4-keto-2-thiazolinylhydrazones are described. H. H. H.

Mononitration of Benzene. K. A. Kobe and J. J. Mills. *Ind. Eng. Chem.*, **45**, 287–291 (Feb. 1953).

Nitration of benzene using an H_2SO_4 : benzene ratio of 1·2, initial H_2SO_4 concn. of 84%, and the theoretical quantity of nitric acid at 60°c. for 40 min. gave mononitrobenzene in $>$ 98% yield. The effect of changing the process variables is shown graphically, and by plotting contour lines of equal yield it is shown that there exists a wide range of H_2SO_4 concn. and temp. in which yields of $>$ 98% can be obtained. W. K. R.

Kinetics and Mechanism of Aromatic Nitration. X—Variation of the Rate of Aromatic Nitration in Sulphuric Acid Media with Composition of the Solvent. R. J. Gillespie and D. G. Norton. *J.C.S.*, 971–979 (March 1953).

Studies in Peroxidase Action. VIII—Oxidation of *p*-Chloroaniline. A Reaction involving Dechlorination. D. C. H. Daniels and B. C. Saunders. *J.C.S.*, 822–826 (March 1953).

The peroxidase oxidation of *p*-chloroaniline at room temperature affords 2-amino-5-*p*-chloroanilinobenzoquinone di-*p*-chloroanil (I) as the main product. When this compound is boiled with acetone, 2-*p*-chloroanilino-5-*iso*propylideneaminobenzoquinone di-*p*-chloroanil is formed. Chloride ion is produced in amount sufficient to account for the production of I. H. H. H.

Preparation of *p*-Methyl- and *p*-Methoxy-anisole from *p*-Toluidine and *p*-Anisidine. S. Yura, K. Uno, and A. Nagasaka. *J. Chem. Soc. Japan, Ind. Chem. Sectn.*, **54**, 231–232 (1951): *Chem. Abs.*, **47**, 2489 (10 March 1953).

p-Toluidine is diazotised with HCl and $NaNO_2$, and converted to the diazonium double salt with $ZnCl_2$. After being washed with methanol, the complex is boiled with methanol to give *p*-methylanisole in 54·2% yield. Similarly the $ZnCl_2$ double salt of diazotised *p*-anisidine, heated in an iron autoclave with methanol at 100–110°C., gives a 41% yield of *p*-methoxyanisole. E. S.

Influence of Conjugation on the Ionisation of Aromatic Amines. N. S. Hush. *J.C.S.*, 684–691 (Feb. 1953).

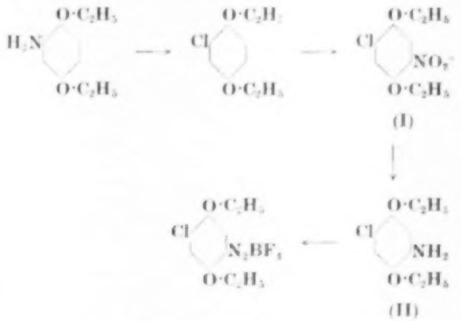
Energy changes attending ionisation of aromatic mono- and di-amines are discussed, and an explanation is given as to why differences in ionisation energy among bases of these types are so much smaller than for proton addition to nuclear nitrogen in isoconjugate heteroaromatic amines. Types of energy change for different ionisations are examined, approximate values of some Coulomb integrals obtained, and energetics of prototropic reactions involving aminium ions considered. The electron densities of 15 dicarbanions are included. H. H. H.

Reaction of Diazonium Salts with Amines. S. Kruger. *J.C.S.*, 700–702 (Feb. 1953).

The relative reactivities of a number of monosubstituted anilines are determined by allowing two aromatic amines to compete for a limited amount of diazonium salt, the relative amounts of diazoamino compound formed being measured. The coupling reaction is found to behave essentially as a nuclear electrophilic one, and could not involve the aminium ion, where the nuclear electron density is decreased to an extremely low level by the positive charge on the nitrogen. H. H. H.

Derivatives of *p*-Diethoxybenzene. I—2-Chloro-1:4-diethoxybenzene-5-diazonium Borofluoride. K. H. Klaassens and C. J. Schoot. *Rec. Trav. chim.*, **72**, 91–93 (Jan. 1953).

2-Chloro-1:4-diethoxybenzene-5-diazonium borofluoride (II) was prepared as follows—



Nitration of the 2-chloro-1:4-diethoxybenzene gave an 83% yield of pure nitro compound (I), the position of the nitro group being confirmed by converting to the dichlorodiethoxybenzene via the amino compound. This was found to be identical with 2:5-dichloro-1:4-diethoxybenzene prepared from benzoquinone and HCl. C. H. R.

Derivatives of *p*-Diethoxybenzene. II—2-Amino-1:4-diethoxybenzene-5-diazonium Borofluoride. K. H. Klaassens and C. J. Schoot. *Rec. Trav. chim.*, **72**, 178–182 (Feb. 1953).

2-Amino-1:4-diethoxybenzene-5-diazonium borofluoride (II) was obtained as follows—

The position of the nitro group in I was proved by replacing the acylamino group with chlorine by the Sandmeyer reaction, when the chlorodiethoxynitrobenzene so obtained was identical with 2-chloro-1:4-diethoxy-5-nitrobenzene described in Part I (cf. previous abstract). C. H. R.

Effects of Substituents and Solvents on the *cis* → *trans* Change of Azobenzene. R. J. W. Le Fèvre and J. Northcott. *J.C.S.*, 867–870 (March 1953).

The rates of geometrical inversion of azobenzene in seven solvents, and of azobenzene together with five *p*-substituted azobenzenes in benzene, are studied by dielectric capacity–time measurements. All show Arrhenius equations similar to those previously found to be applicable to aromatic diazocyanides (cf. *J.C.S.*, 944 (1949)). H. H. H.

***o*-Mercapto-azo Compounds. III—Action of Thiocyanic Acid on Diazotised *o*-Nitroarylamines.** A. Burawoy and C. Turner. *J.C.S.*, 959–962 (March 1953).

The nitro group in the diazonium salts from 1-nitro-2- and 2-nitro-1-naphthylamine is replaced by a thiocyanato group in presence of thiocyanic acid. The thiocyanatodiazonium salts formed couple with *β*-naphthol to form azo compounds, which are converted by alkali into disulphides, and these are reduced by sodium sulphide to thiols. H. H. H.

Bromination of Compounds containing two Aromatic Nuclei. XII—Bromination of Arylamides of 2-Methoxy-5-nitrobenzoic Acid. G. V. Jadhav and P. G. Nerlekar. *J. Indian Chem. Soc.*, **29**, 765–768 (Oct. 1952).

Bromination of the anilide, *o*-, *m*-, *p*-toluidides, *o*-, *m*-, *p*-nitroanilides, *o*-, *p*-anisidides, *p*-phenetidide, and *β*-naphthylamide of 2-methoxy-5-nitrobenzoic acid was carried out under different conditions, when bromination occurred only in the basic residue. In a few cases the bromo derivatives may be hydrolysed by boiling NaOH, giving bromoamines and 5-nitrosalicylic acid. A. J.

Synthesis of 2-Amino-5-aminomethyl-4-methylthiazole. K. Murata and H. Ikehata. *Bull. Chem. Soc. Japan*, **25**, 352–353 (Oct. 1952).

2-Amino-5-cyano-4-methylthiazole (I) is reduced by means of Raney nickel in absolute methanol and 25 atm. H_2 in 2 hr. at 10–15° c. After inorganic impurities have been separated, 2-amino-5-aminomethyl-4-methylthiazole hydrochloride is obtained by saturating the filtrate with HCl gas and cooling. Reduction of I with palladium and H_2, by electrolysis, and with lithium aluminium hydride is unsatisfactory. The product is assumed to be the reduction product of an azo dye from aneurin (vitamin B_1). A. J.

Synthesis of Water-repellent Dyes. C. C. DeWitt and P. D. Shroff. *Ind. Eng. Chem.*, **45**, 302–307 (Feb. 1953).

The water repellency of wool and cotton dyed with eight azoic dyes containing various long-chain *n*-alkyl substituents and two basic dyes, octyl-malachite green and octyl-rosaniline, when tested by the Draves sinking time method, was much greater than when dyed with the corresponding unsubstituted dyes. Water repellency increased with increasing length of the alkyl chain and with the number of such alkyl groups in the dye molecule. The preparation of the substituted dyes is described. In comparison with the corresponding unsubstituted dyes, they had greater oil solubility and the colour of the basic dyes was much duller, whilst the azoic dyes gave generally paler and sometimes duller shades. W. K. R.

Acylation and Allied Reactions catalysed by Strong Acids. IX—Ease of Formation and Reactions of the Diphenylmethyl and some Triarylmethyl Cations. H. Burton and G. W. H. Cheeseman. *J.C.S.*, 832–837 (March 1953).

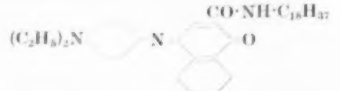
Substitution reactions are described of the diphenylmethyl cation, which is prepared from benzhydrol (diphenylmethanol) and perchloric acid. Various triarylmethyl cations are also described and shown to be active entities. A novel reaction of the tri-*p*-methoxyphenylmethyl cation with nitromethane is discussed, which leads to 1:1:1-tri-*p*-methoxyphenyl-2-nitroethane. H. H. H.

Absorption and Luminescence Spectra of Triphenylmethane Dyes. P. P. Feofilov and I. G. Faerman. *Doklady Akad. Nauk S.S.S.R.*, **87**, 931–934 (21 Dec. 1952).

Absorption and fluorescence spectra are determined in the visible region for 13 triphenylmethane dyes in glycerol soln. at ~ -80 c., and observations are made also on the relation between the degree of polarisation of the fluorescent emission and the wavelength of the exciting radiation. Previous work by this school has indicated that the subsidiary max. in the main absorption band of a dye of this type having three auxochromes and a symmetrical or almost symmetrical molecular structure, e.g. Crystal Violet, arises not from vibrational fine structure or the presence of polymeric forms, but from a second electronic transition, the dye molecule being regarded as a group of three oscillators—two alike, and the third somewhat modified, probably owing to its association with the anion. It is now shown that for these dyes the degree of polarisation of the fluorescent emission varies greatly with the wavelength of the exciting radiation, and the fluorescence spectrum does not show the theoretically required mirror-image relationship with the absorption spectrum. It is considered, however, that this relationship does in fact hold between the fluorescence spectrum and the principal, longer-wave component of the main absorption band. On this assumption it is possible to resolve the absorption band into its two components. Each of the superimposed absorption bands is associated with its own specific polarisation effect in the fluorescence spectrum, and by considering the superposition of these effects a relation is derived between the degree of polarisation of the fluorescent emission and the wavelength of the exciting radiation; it agrees fairly well with the observed polarisation spectrum. Dyes having only two auxochromes, e.g. Malachite Green, have no subsidiary maxima, give the mirror-image absorption–fluorescence relation, and show no appreciable variation in degree of fluorescence polarisation with variation in the wavelength of the exciting radiation. A. E. S.

Quantitative Study of Formation of Blue Dye in Colour Development. Yu. B. Vilensky and S. A. Bongard. *J. Appl. Chem. U.S.S.R.*, **26**, 89–95 (Jan. 1953).

The blue dye—



formed in photographic colour development from the octadecylamide of 1-hydroxy-4-sulphonaphthalene-2-carboxylic acid (non-diffusing component) and *NN*-diethyl-*p*-phenylenediamine, is shown to conform to Beer's law, both in soln. in various solvents and in the condition in which it is formed in a gelatin layer. It is then shown absorptiometrically that for each g.-atom of Ag formed in the development process the amount of dye produced simultaneously is 0·47 mole (94% of theoretical yield). A. E. S.

Colour Reactions of α-Ionone and of 5-Oxo-α-ionone with Alkali. P. Karrer and U. Blass. *Helv. Chim. Acta*, **36**, 463–466 (March 1953).

Addition of aqueous alkali to alcoholic solutions of *α*-ionone and of 5-oxo-*α*-ionone gives a red colour owing to salt formation; the absorption spectrum of each red salt has a maximum at 510 mμ. Since *β*-ionone does not give a similar colour reaction, the latter serves for the estimation of small quantities of *α*- in *β*-ionone. H. H. H.

Sesquiterpenes and Azulenes. CV—Polarographic Reduction of Azulenes—I. L. H. Chopard-dit-Jean and E. Heilbronner. *Helv. Chim. Acta*, **36**, 144–160 (Feb. 1953).

5:5′-Dithiazolyl. M. Erne, L. Herzfeld, B. Prijs, and H. Erlenmeyer. *Helv. Chim. Acta*, **36**, 354–357 (March 1953).

2:2′-Hydrazothiazole when heated with phthalic anhydride gives 2:2′-diphthalimido-5:5′-dithiazolyl, which hydrolyses in two stages, viz. alkaline to the *o*-carboxybenzoyl derivative and then acid to 2:2′-diamino-5:5′-dithiazolyl. The latter when bisdiazotised (tetrazotised) and treated with hypophosphorous acid gives 5:5′-dithiazolyl in 37% yield. This synthesis completes the set of possible dithiazolyls. H. H. H.

Spectroscopic Properties of Conjugated Systems. K. Shibata. *Bull. Chem. Soc. Japan*, **25**, 378–385 (Dec. 1952).

The absorption spectra of a large number of conjugated compounds have been measured in ethanol soln. For symmetrical cyanine dyes and polyenes the positions of the absorption maxima may be expressed by the equation—

$$\lambda^2 = \frac{n}{k + k'n}$$

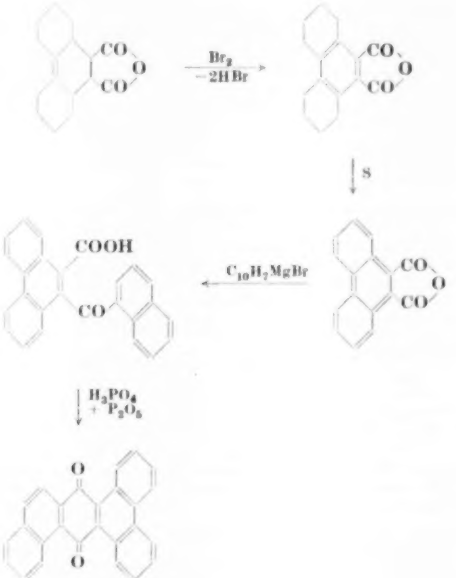
(k and k' = constants; n = "colour factor" of the molecule, defined as the sum of the number of bonds in the conjugated chain plus a colour factor for each of the terminal nuclei). Colour factors for eighteen terminal nuclei are given. The rule does not apply to substituted thiobenzophenones, styryl dyes, or unsymmetrical cyanine dyes. A. J.

Low-temperature Photochromism and its relation to Thermochromism. Y. Hirshberg and E. Fischer. *J.C.S.*, 629–636 (Feb. 1953).

When solutions of dianthrone, dixanthylen, xanthylideneanthrone, and their derivatives are irradiated at −150° to −70° c. with light of $\lambda > 450$ mμ., reversible formation of coloured modifications takes place (photochromism). Comparison of the visible and near ultraviolet absorption spectra of these coloured modifications with the spectra of the coloured forms obtained reversibly on heating their solutions (thermochromism) shows identity, and that low-temperature irradiation may cause considerable or even complete conversion into the coloured form. The relation between photo- and thermo-chromism is discussed, and tentative conclusions are drawn with respect to the mechanism of photochromism and the electronic and atomic configuration of the coloured and colourless modifications. H. H. H.

Syntheses of Carcinogenic Hydrocarbons. X—9:10-Dimethyl-1:2:3:4:5:6-tribenzanthracene [and 1:2:3:4:5:6-Tribenzanthraquinone]. P. Lambert and R. H. Martin. *Bull. Soc. chim. Belg.*, **61**, 513–523 (Oct.–Nov. 1952).

1:2:3:4:5:6-Tribenzanthraquinone (I) was prepared from the Diels–Alder adduct of di*cyclo*hexenyl and maleic anhydride—



(I)

The final ring closure, which did not take place with other common agents, e.g. $ClSO_3H$, gave only very poor yields. A better yield of I was obtained together with the *o*-quinone (II) and the diquinone (III) by oxidation of 1:2:3:4:5:6-tribenzanthracene with sodium dichromate. 9:10-Dimethyl-1:2:3:4:5:6-tribenzanthracene was obtained from the corresponding 9:10-quinone by reaction with methylmagnesium iodide.

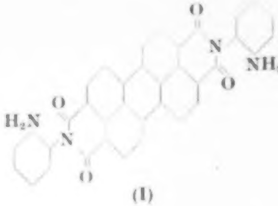
(II)

(III)

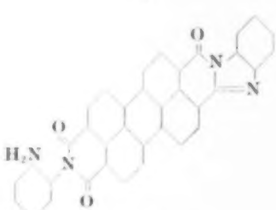
C. H. R.

Vat Dyes of the Acenaphthene Series. IV—Condensation of Perylenetetracarboxylic Anhydride with o-Phenylenediamine. T. Maki and H. Hashimoto. *Bull. Chem. Soc. Japan*, **25**, 411–413 (Dec. 1952).

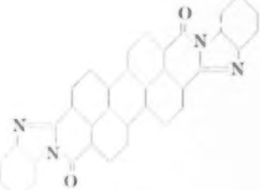
Condensation of perylenetetracarboxylic acid with *o*-phenylenediamine at 160°, 190°, and > 200° c. yields I, II, and III respectively as main products. II is readily sol. in alkaline hydrosulphite and 90% H_2SO_4, and dyes cotton a deep violet from a violet-red vat. It is designated Acenaphthene Violet. The dyeings have light fastness of 8, washing fastness 4–5, and fastness to chlorine 5. The free amino group may be diazotised, and when coupled on the fibre with β-naphthol the colour becomes redder and the light fastness falls to 2. I and III are insol. in alkaline hydrosulphite. I may also be prepared by condensation of perylenetetracarboxylic anhydride with *o*-nitroaniline followed by reduction at 60° c. with alkaline hydrosulphite containing Na_2S. I is converted to II by boiling with nitrobenzene for 1–1·5 hr., and II to III by boiling with nitrobenzene for 5 hr.



(I)



(II)



(III)

A. J.

Chemistry of Indanthrone. VIII—3:3′-Dimethyl Derivatives of Indanthrone and Flavanthrone. W. Bradley and H. E. Nursten. *J.C.S.*, 924–927 (March 1953).

3:3′-Dimethylindanthrone (I) is shown to resemble indanthrone (II) and to differ from 3:3′-di-*tert.*-butylindanthrone (III), in both properties and methods of preparation. The effect of *tert.*-butyl groups in promoting the formation of flavanthrone derivatives and in restraining the formation of the corresponding indanthrone compounds is emphasised. I is less stable than II, but more stable than III, towards illumination in chlorobenzene; the progression follows that of ease of electron release in the series H, CH_3, $C(CH_3)_3$. The solubilities of I, II, and III in chlorobenzene increase in the same order. Compared with *NN′*-dimethylindanthrone, I is much less soluble in organic solvents, a further confirmation of the occurrence of intermolecular hydrogen bonding in II and its simple nuclear-substituted derivatives. H. H. H.

Synthesis of Vat Dyes of the Pyrazoleanthrone Series. I—Synthesis of Pyrazoleanthrone. T. Maki, T. Akamatsu, and M. Maezwa. *J. Chem. Soc. Japan, Ind. Chem. Sectn.*, **54**, 244–246 (1951): *Chem. Abs.*, **47**, 2490 (10 March 1953).

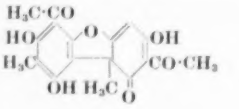
When potassium 2-1′-anthraquinonylhydrazine-sulphonate (I—1 part) is heated with conc. H_2SO_4 (8) at 100° c. for 3 hr., pyrazoleanthrone (II) is obtained in 99·97% yield. I is quantitatively converted into 1-anthraquinonylhydrazine hydrochloride by heating with 23·3% HCl. The corresponding sulphate is obtained by heating with 35% H_2SO_4. II is produced in 98–99% yield from these hydrazine salts by treating with conc. H_2SO_4 at 100° c. C. O. C.

Constitutional Formula of 2-Thionaphthen-7′-(1′-methoxy)acenaphthenylindigo. S. K. Guha. *J. Indian Chem. Soc.*, **29**, 787–788 (Oct. 1952).

1′-Methoxy derivatives of thioindigoid vat dyes of the acenaphthenequinone series are difficult to reduce satisfactorily in alkaline hydrosulphite, and give only light shades on cotton. It is suggested that these dyes have the *trans* structure, and the reduction behaviour is due to steric hindrance of the 8′-carbonyl by the 1′-methoxy group. A. J.

Constitution of Usnic Acid. D. H. R. Barton and T. Bruun. *J.C.S.*, 603–609 (Feb. 1953).

Ozonolysis of usnic acid anhydrophenylhydrazone diacetate affords 3-methyl-1-phenylpyrazole-4:5-dicarboxylic acid and a compound $(C_{16}H_{15}O_7)_2$; the latter also results from the oxidative coupling of the intermediate 4:6-diacetoxy-7-acetyl-5-methylcoumaran-2-one, and by oxidation of usnic acid diacetate with $KMnO_4$. The degradation of the above hydrazone by KOH in methanol and ethanol is reported, and the significance of the various results assessed in terms of Robertson's usnic acid formula (I).



(I)

H. H. H.

Chemistry of Mould Metabolites. I—Isolation and Characterisation of a Red Pigment from *Coriolus sanguineus* (Fr.). G. W. K. Cavill, B. J. Ralph, J. R. Tetaz, and R. L. Werner. *J.C.S.*, 525–529 (Feb. 1953).

The bright-red wood-rotting fungus, *Coriolus sanguineus* (Fr.), found on decaying pines and eucalyptus in the natural bushlands close to Sydney, contains a compound, $C_{14}H_{10}O_5N_2$, believed to be identical with Lemberg's polystictin and Gripenberg's cinnabarin; this contains an acidic hydroxyl group, an amide group, and possibly an ether link. The basic skeleton is of a polycyclic unsaturated type containing a quinonoid system and heterocyclic nitrogen. H. H. H.

Pigments of *Bixa orellana*—Annatto. W. Diemair, H. Janecke, and D. Heusser. *Naturwissenschaften*, **39**, 211 (1952): *Chem. Abs.*, **47**, 2838 (25 March 1953).

Annatto prepared from *Bixa orellana* seeds contains several other pigments besides the principal one, bixin. After saponification of the bixin, it was separated from these pigments, and the latter were separated in a hypo- and an epi-phase. The epiphase with a dark red, thick, oily residue was separated on $Cu(OH)_2$ by chromatography. Six pigments appeared—(1) orange, maximum absorption in hexane 454–455, 487 mμ.; (2) rose orange 453, 486; (3) rose red 452, 471–472; (4) orange 451; (5) brown orange 420, 444; (6) bright yellow 375, 400, 425. Zones 1–4 are distinctly different in intensity and colour; the pigment of zone 6 is probably ζ-carotene. No separation of the hypophase has so far succeeded; the curve is flat, max. in CS_2 at ca. 450 mμ. All pigments give the carotene reactions. The high Fe content of extracts in organic solvents is noteworthy. C. O. C.

Relation between Spectral Changes and pH of the Anthocyanin Pelargonidin 3-Monoglucoside. E. Sondheimer. *J. Amer. Chem. Soc.*, **75**, 1507–1508 (20 March 1953).

The predominant effect of increasing hydrogen ion activity on the spectral properties of pelargonidin 3-monoglucoside is increase in intensity of absorption in the visible region. Furthermore, on addition of water to unbuffered benzopyrylium salt solutions decrease in light absorption is observed which is greater than can be accounted for solely by dilution effects. Evidence is given indicating that these effects are caused by there being an equilibrium between hydronium ions, a red modification R^+, and a colourless form ROH of the anthocyanin.

C. O. C.

Synthesis of Chrysin and of other Natural Hydroxyflavone Dyes. C. Mentzer and D. Pillon. *Compt. rend. Acad. Sci. Paris*, **234**, 444–446 (1952): *Chem. Abs.*, **47**, 2172 (10 March 1953).

Phloroglucinol (7·77 g.) and $C_6H_5{\cdot}CH_2{\cdot}COOC_2H_5$ (7·68) kept for 1·5 hr. at 240–250°c., cooled, taken up in 5% NaOH, extracted with ether, and pptd. with acid, the ppt. (5·65) being sublimed at 250–300°c./0·01–0·03 mm., and the sublimate (3·15) crystallised from alcohol, gave a 20% yield of chrysin. Acacetin (21%) and 7-hydroxyflavone (25%) were similarly prepared. C. O. C.

Dyeing and Tanning Components in Young Fustic from Venezia Giulia. L. Ferro. *Cuoio, Pelli, Mat. concianti*, **28**, 359–367 (1952): *Chem. Abs.*, **47**, 2526 (10 March 1953).

The powdered extract of the wood of *Rhus cotinus* contains 44·3% tannins, 44·8% non-tannins, 1·2% insoluble matter, 9·7% water, and 9·39% ash. The tannins consist of about 40% catechol and 60% pyrogallol tannins. C. O. C.

Physical Properties of White Pigments with particular reference to Titanium Dioxide. W. Hughes. *J. Oil & Col. Chem. Assocn.*, **35**, 535–554 (Nov. 1952).

The scattering of light by fine particles is discussed, and it is shown that there is an optimum particle size for max. scattering. Light absorption characteristics and the effect of trace impurities within the crystal lattice are considered in relation to tone and photochemical activity. The influence of the manufacturing process on particle size and shape is considered. A. J.

Crystal Structure of Realgar. T. Ito, N. Morimoto, and R. Sadanaga. *Acta Cryst.*, **5**, 775–782 (1952): *Chem. Abs.*, **47**, 2566 (25 March 1953).

Realgar, AsS, is monoclinic with unit cells containing 16 AsS per cell, the unit cell containing separate As_4S_4 molecules very similar to those found in the vapour. The relation to the structure of orpiment is discussed.

C. O. C.

Cadmium–Selenium Red—I. T. Yamauchi and Y. Endo. *J. Ceram. Assocn. Japan*, **60**, 417–421 (1952): *Chem. Abs.*, **47**, 2505 (10 March 1953).

Roasting of $CdCO_3$ + Se + S (S : Se = 1–2) at 550°c. for 10–15 min. and of CdS + Se (Se 14–20%) at 450–650°c. for 10–20 min. yielded good pigments. X-Ray study showed that cadmium–selenium red is a solid solution of α-CdS and CdSe. Increase of CdSe in the solid soln. causes darkening of the red. C. O. C.

X-Ray Study of the Thermal Decomposition of Prussian Blue. J. J. Trillat and S. Barbezat. *Peintures, Pigments, Vernis*, **28**, 604–606 (1952): *Chem. Abs.*, **47**, 2999 (25 March 1953).

Heating in absence of air at $\not>$ 200°c. causes no change in properties. Heating in presence of air at $\not>$ 160°c. also causes no change, but at 200°c. partial conversion occurs; at 250°c. an amorphous non-magnetic product forms, perhaps FeO; further heating gives Fe_3O_4 and Fe_2O_3; at 300°c. instantaneous conversion to Fe_3O_4 and Fe_2O_3 occurs. When the pigment is incorporated in alkyd resin, heating at $\not>$ 150°c. begins to char the resin; decomposition of resin is marked at 200°c., but the pigment is unchanged. Heating at 300°c. for 6 min. gives a non-magnetic product still showing a feeble Prussian blue pattern. C. O. C.

Physics of Crystal Phosphors. F. Stöckmann. *Naturwissenschaften*, **39**, 226–233, 246–254 (1952): *Chem. Abs.*, **47**, 2587 (25 March 1953).

A review dealing with SrS and ZnS phosphors with two activators, photoelectric conduction, photography, and quantitative relations in phosphorescence and fluorescence; 63 references. C. O. C.

Cream-coloured Titanium Dioxide Pigment from Ilmenite. K. V. Nayar. *Bull. Central Research Inst. Univ. Travancore*, **11**, 106–108 (1952): *Chem. Abs.*, **47**, 2505 (10 March 1953).

Ilmenite was placed in a porcelain cylinder having gas-tight joints and heated by a current passed through a nichrome wire wound around the cylinder. The cylinder was revolved, and H_2S passed in. The iron sulphate was washed off with dil. acid, and excess H_2S absorbed in a suspension of MgO. The product was a cream-coloured TiO_2. C. O. C.

Hiding Power of Pigments as a Function of their Particle Size. W. Lützkendorf. *Farbe und Lack*, **59**, 7–16 (1953): *Chem. Abs.*, **47**, 2999 (25 March 1953).

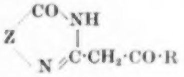
Electron-microscopic measurements show that the hiding power of a pigment increases with decreasing particle size (Ebler's equation) until the latter falls below the wavelength of the light which the pigment reflects or absorbs; the pigment then becomes colloidal or translucent, and finally becomes transparent when its particle size falls below half that wavelength. This is demonstrated with water-soluble Paris Blue, Heliogen Blue B, Chrome

Oxide Green GX, Chrome Oxide Hydrate Green Le 70, Hansa Yellow G, Hansa Yellow G Transparent, Lake Red toners, Molybdate Red G (75% $PbCrO_4$, 15% Pb molybdate, 10% $PbSO_4$), Cadmopur Red BB, Cadmofixe Red BB, Helio Red RMT extra, TiO_2, lithopone, Green-label ZnO, and reactive ZnO. The division of colouring matters into dyes, colloids, and pigments is discussed on the basis of their solubility. Polar colouring matters, e.g. basic, acid, and direct cotton dyes, are soluble in polar vehicles, but insoluble and capable of hiding in non-polar vehicles. Non-polar pigments are non-hiding in non-polar vehicles, but insoluble and hiding in polar vehicles. Both polar and non-polar colouring matters are non-hiding in such vehicles as celluloid or Bakelite. C. O. C.

PATENTS

Colour Couplers. Gevaert. *BP* 689,023

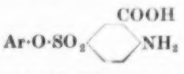
Compounds of formula—



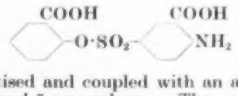
(Z = arylene; CO·R = acyl, ester, amide, hydrazide, or hydroxamic acid group) are colour couplers for yellow dyes in three-colour photography. C. O. C.

Yellow, Metallisable, Monoazo, Pyrazolone Acid Dyes. Ciba. *BP* 688,850

Aryl 5-sulphonates of anthranilic acid—



(Ar preferably contains COOH *ortho* to its point of attachment to the O atom) are diazotised and coupled with suitable 5-pyrazolones to yield yellow dyes, which may be metallised (particularly with Cr) in substance, in the dye-bath, or on the fibre. Thus *o*-chlorobenzoic acid is stirred into cold chlorosulphonic acid and heated to 95–100°c. to yield the 5-sulphonyl chloride, which is treated with cold aq. salicylic acid in presence of NaOH to give the *o*-carboxyphenyl ester. Heating with NH_3 in presence of Cu powder in an autoclave at 125–130°c. replaces Cl by NH_2, giving—



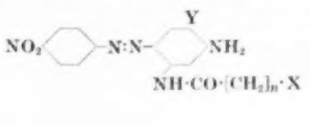
which is diazotised and coupled with an alkaline soln. of 3-methyl-1-phenyl-5-pyrazolone. The product is a brownish-yellow afterchrome or metachrome monoazo dye. E. S.

Solubilised Disperse-type Monoazo Dyes for Acetate Rayon and Nylon. IC. *USP* 2,606,896

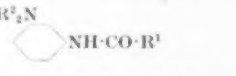
Diazotising primary amines free from SO_3H and COOH groups in presence of phenol(or naphthalene)sulphonic acid–formaldehyde condensates, and then coupling with suitable coupling components also free from SO_3H and COOH groups, produces disperse-type dyes in a solubilised form. Thus 2:4-dinitroaniline (18·3 g.) is suspended in a 35% aq. soln. of a phenolsulphonic acid–formaldehyde condensate (ca. 2000 g.), and conc. H_2SO_4 (ca. 30 c.c.) added. After stirring for 16 hr., the formation of a soluble addition compound is complete. After cooling to 0–5°c., sodium nitrite (7·2 g.) is added and diazotisation completed by stirring for several hours. The clear brownish-yellow diazo solution so obtained is coupled with *NN*-bis-β-hydroxyethyl-*m*-toluidine to give an addition compound of the monoazo dye which is in complete solution and may be used directly for dyeing acetate rayon or nylon. E. S.

Dischargeable Developed Blues on Acetate Rayon. Celanese Corpn. of America. *BP* 690,173 *USP* 2,606,898

Dischargeable deep blues are produced on acetate rayon by dyeing with a monoazo compound—



(n = 0–4; X = COOH or $CO·NH_2$; Y = H, CH_3, C_2H_5, C_3H_7, $CH_3·O$, $C_2H_5·O$, or $C_3H_7·O$), diazotising on the fibre, and coupling with a developer, preferably of the structure—



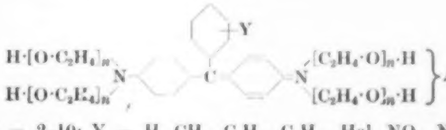
(R^1 = H, CH_3, C_2H_5, or C_3H_7; R^2 = CH_3, C_2H_5, C_3H_7, C_2H_4OH, C_3H_6OH, or $C_3H_5(OH)_2$). Thus diazotised *p*-nitroaniline is coupled with 3-amino-4-methoxyoxanilic acid to yield a monoazo dye which, dyed on acetate rayon from a soap bath, diazotised on the fibre, and coupled with *m*-bishydroxyethylaminoacetanilide, yields navy blues which are dischargeable to white on reduction with sodium formaldehyde-sulphoxylate. E. S.

Crystal Violet. DuP. *USP* 2,600,649

Crystal violet (*C.I.* 681) having good properties when used in duplicating inks is prepared by treating crystal violets containing Zn with an aq. soln. of a ferrocyanide (0·25–1·0 mol. per Zn atom) in water or aq. alcohol. R. K. F.

Triphenylmethane Dyes. General Aniline. *USP* 2,598,660

Violet to green basic dyes of formula—



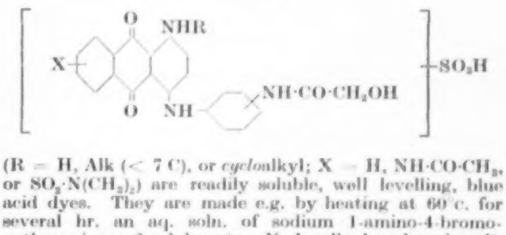
(n = 2–10; Y = H, CH_3, C_2H_5, C_3H_7, Hal, NO_2, NH_2, NR^1R^2, SO_3H, COOH, COOAlk, or O·Alk; A = anion), useful for photographic filter layers, printing inks, plastics, and lacquers, are made by condensing an aromatic aldehyde with an *NN*-bis(hydroxyalkylpolyoxyalkyl)aniline, and then oxidising with PbO_2 or MnO_2. Thus, *NN*-bis(8-hydroxy-3:6-dioxaoctyl)aniline (from aniline and ethylene oxide—*USP* 2,161,322) is heated for 24 hr. at 100°c. with benzaldehyde and HCl. The resulting leuco compound, after being separated, is oxidised by pasting with PbO_2 at 0–5°c. R. K. F.

Halogenoaminoanthraquinones. Basf. *BP* 688,810

Aminoanthraquinones are halogenated in $AlCl_3$ containing a m.p. depressant, e.g. NaCl, Na_2SO_4, or KCl, at 60–130°c. Thus 2-amino-3-bromoanthraquinone is obtained by adding Br_2 slowly to a soln. of 2-aminoanthraquinone in a mixture of $AlCl_3$ (200 parts) and Na_2SO_4 (30) at 125–130°c. R. K. F.

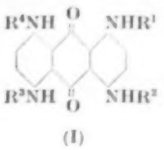
1 - Amino - 4 - glycolloylaminophenylaminoanthra - quinonesulphonic Acids—Wool Dyes. FBy. *BP* 690,096

Compounds of general formula—

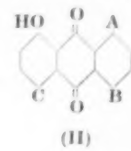


(R = H, Alk (< 7 C), or *cyclo*alkyl; X = H, $NH·CO·CH_3$, or $SO_2·N(CH_3)_2$) are readily soluble, well levelling, blue acid dyes. They are made e.g. by heating at 60°c. for several hr. an aq. soln. of sodium 1-amino-4-bromoanthraquinone-2-sulphonate, *N*-glycolloyl-*p*-phenylenediamine, $NaHCO_3$, and Cu_2Cl_2. R. K. F.

1:4:5:8-Tetra-aminoanthraquinones. Eastman Kodak Co. *USP* 2,611,772



(I)

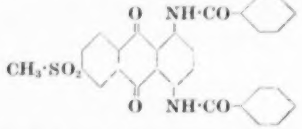


(II)

Compounds of formula I (R^1, R^2, R^3, and R^4 = Alk, hydroxyalkyl, alkoxyalkyl, *NN*-dialkylaminoalkyl, sulphoalkyl, carboxyalkyl, aralkyl, or *cyclo*alkyl) are obtained by treating a compound of formula II (A, B, and C = OH or NHR) with one of formula $R'{\cdot}NH_2$ (R and R' = R^1, R^2, R^3, or R^4) in absence of an oxidising agent for the leuco anthraquinone compound. They are useful for colouring petrol and as filter dyes for absorbing infrared rays. C. O. C.

Acylaminoanthraquinonyl Alkyl Sulphones—Vat Dyes. Ciba. *BP* 689,279

1-Acylamino- or 1:4-bisacylamino-anthraquinones carrying a 6- or 7-alkylsulphonyl group are yellow or red vat dyes. They are made by either (*a*) acylating the corresponding amino or diamino sulphone, itself prepared by nitrating and reducing a 2-alkyl sulphone, or (*b*) oxidising with H_2O_2 in chlorinated acetic acid the acylamino or diacylamino 6(or 7)-alkylthio compound, itself made by treating the corresponding amino or diamino 6(or 7)-halogeno derivative with an alkali-metal hydrosulphide. Thus the dye—



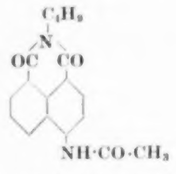
is obtained by heating 1:4-diamino-6-methylsulphonyl-anthraquinone with benzoyl chloride in nitrobenzene at 135–140°c. R. K. F.

Sulphurised Anthraquinone Vat Dyes. J. M. Danner and W. Zerweck. *BP* 688,651

Brown vat dyes are obtained by treating nitrogen-free quinones containing six condensed benzene rings, with or without rings of 5 C, in molten $AlCl_3$–alkali-metal chloride mixtures with SO_2. Thus, all parts being by weight, a dye containing 8% S and 8% Cl is produced by passing SO_2 for 6 hr. at 140–150°c. through anthanthrone (40) in a mixture of $AlCl_3$ (200) and NaCl (33). R. K. F.

4-Acetylamino-*N*-butyl-1:8-naphthalimide. General Aniline. *USP* 2,600,080

4-Nitronaphthalic anhydride is refluxed in acetic acid with *n*-butylamine until dissolved. After cooling to 100°c., the NO_2 is reduced by adding Fe powder, and the resulting NH_2 acetylated by adding acetic anhydride and refluxing. The resulting—



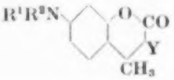
and related derivatives are yellow dyes for organic solvents, the solutions of which fluoresce blue in ultraviolet radiation. R. K. F.

Acedianthrone–Carbazole Vat Dyes. CFM. *BP* 690,006

Aminoanthraquinones are condensed with *aaaa*-tetrahalogenoacedianthrones by the process of *BP* 410,552 (J.S.D.C., **50**, 331 (1934)), the resulting anthrimides being simultaneously cyclised to the corresponding carbazoles, which are brown to olive vat dyes. Thus an *aaaa*-tetrachloroacedianthrone (1 mol.—from 1:8-dichloroanthrone) and 1-amino-5-benzoylaminoanthraquinone (3 mol.) are stirred at 50–55°c. for 3 hr. in chlorosulphonic acid. R. K. F.

Fluorescent Brightening Agents for use in Dry-cleaning Solvents. S. *BP* 689,708

Compounds of formula—



(R^1 and R^2 = H, CH_3, or C_2H_5; Y = H or CH_3) are fluorescent brightening agents applicable from water-insoluble organic solvents but not showing their brightening effect until the treated material has been steamed. C. O. C.

Sulphonated Copper Phthalocyanine. Eastman Kodak Co. *USP* 2,600,377

Sulphonated copper phthalocyanine, specially suitable for use in the imbibition process of colour photography, i.e. having a maximum light absorption at 668 mμ., is prepared by sulphonating in 15% oleum containing mercuric sulphate at 170–175°c., diluting with water, and separating at pH 5 as the guanidine salt, which is finally converted to the Na salt by means of Na acetate. R. K. F.

Sulphonated Phthalocyanines. Basf. *BP* 688,790

Sulphonating agents, e.g. H_2SO_4, $ClSO_3H$, SO_2Cl_2, are trickled or sprayed on to a phthalocyanine at 80–220°c. in amounts which allow sulphonation to take place in the solid phase. Thus, all parts being by weight, cobalt phthalocyanine (113) and $ClSO_3H$ (34) are stirred together for 30 min. at 200°c. The products are vat dyes or, where the degree of sulphonation is higher, may be converted to their water-insoluble alkaline-earth derivatives, which are pigments. R. K. F.

Phthalocyanine Vat Dyes. Basf. *BP* 688,784

Iron, nickel, or cobalt phthalocyanines are treated with phosgene, oxalyl chloride, or sulphuryl chloride under conditions that give products soluble in aq. alkaline hydrosulphite but insoluble in aq. alkali-metal hydroxide. These products after saponification are blue vat dyes. The reaction is carried out in $AlCl_3$–NaCl melts at 110–150°c., and the vat dyes resulting after boiling in aq. HCl to saponify the acid chloride groups contain one COOH per 1–4 mol. of dye or one SO_3H per 2–120 mol. of dye.

BP 688,785

The metal phthalocyanines are treated with 1–4 mol. of a halogenated aliphatic acid, e.g. chloroacetic acid, per mol. of phthalocyanine in an inert solvent, e.g. trichlorobenzene, containing $AlCl_3$ or $FeCl_3$ at 180–200°c. until a sample is soluble in aq. alkaline hydrosulphite but insoluble in aq. alkali-metal hydroxide.

BP 688,786

An *o*-dicarboxylic acid or anhydride (3 mol.) is heated at 140–200°c. together with $<$ 1 mol. of an *o*-dicarboxylic acid containing one SO_3H, SO_2Cl, or $SO_2{\cdot}NH_2$ group, or with $<$ 3 mol. of an *o*-dicarboxylic acid containing a further COOH group, in the presence of a "heavy" metal or its salt, e.g. $CoCl_2$, an N-supplying substance, e.g. urea, and a catalyst, e.g. ammonium molybdate. The resulting products vat in aq. alkaline hydrosulphite but are insoluble in aq. alkali-metal hydroxides. R. K. F.

Halogenomethyl-phthalocyanines. Basf. *BP* 689,153

Halogenomethyl groups are introduced into phthalocyanines by treating them with dichloro- or dibromodimethyl ether (or mixtures forming them, e.g. paraformaldehyde and HCl) in sulphuric acid or one of its fusible derivatives. Thus copper phthalocyanine (30 parts by weight) and paraformaldehyde (60) are heated at 90°c. for 24 hr. in H_2SO_4 (400) while HCl is led in. R. K. F.

Tetra-azaporphin Pigments. ICI. *BP* 688,768

In the phthalocyanine synthesis, part of the phthalic acid derivatives is replaced by maleic acid derivatives or alkyl- or *cyclo*alkyl-substituted maleic acid derivatives to give redder colours than those of the corresponding true phthalocyanines. Thus dimethylmaleic anhydride, phthalic anhydride, urea, anhydrous nickel chloride, and ammonium molybdate are heated for 4 hr. at 140°c. in nitrobenzene. The solvent is removed by steam-distilling after adding HCl, and the product extracted with alkali.

BP 689,387

Tetra-azaporphins containing no aromatic residue are prepared by similar methods from maleic dinitrile or alkyl- or *cyclo*alkyl-substituted maleic or fumaric dinitriles only. They, too, are pigments which are redder than the corresponding phthalocyanines.

BP 689,388

In the preparation of compounds described in *BP* 689,387 (above) the free acids or their functional derivatives are used instead of the corresponding dinitriles.

BP 689,389

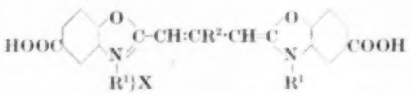
The methods of the two previous patents are used to prepare the corresponding nickel and cobalt tetra-aza-porphins, which are redder than those containing other common metals. R. K. F.

Complexes related to Cobalt Phthalocyanine. FBy. *BP* 687,655

Brown cobalt compounds which are converted to cobalt phthalocyanine by reducing and then oxidising are obtained by heating, with or without a solvent, phthalic anhydride, phthalimide, or mono-iminophthalimide with cobalt salts, ammonium molybdate, and urea or biuret at 140–190° c. The reaction mass is treated with caustic alkali to remove cobalt phthalocyanine, which remains undissolved. The product obtained by acidifying the alkaline filtrate may be incorporated in a printing paste containing a reducing agent, e.g. hydrazine sulphate, which, on application to e.g. cotton followed by steaming, produces blue prints consisting of cobalt phthalocyanine fixed on the fibre. R. K. F.

Benzoxazole Carbocyanine Dyes. DuP. *USP* 2,609,371

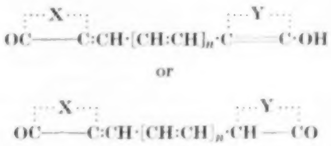
Dyes of formula—



(R^1 = Alk of 1–12 C or benzyl; R^2 = hydrocarbon radical; X = acid radical) are produced from 2-methyl-5-carboxybenzoxazole by converting it into a *cyclo*ammonium salt and treating this salt with an orthoester of a carboxylic acid. They have good sensitising properties and leave no residual stain after development, etc. C. O. C.

Unsymmetrical Oxonol Dyes. Eastman Kodak Co. *USP* 2,611,696

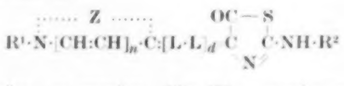
Dyes of formula—



(X = atoms to complete a barbituric or thiobarbituric acid, *iso*oxazolone, or indanedione nucleus; Y = atoms to complete a pyrazolone nucleus; n = 0–2) have excellent photographic filter and antihalation properties. C. O. C.

***mero*Cyanine Dyes.** Kodak. *BP* 689,025

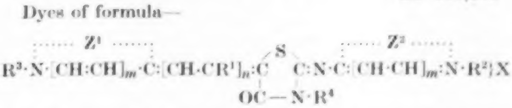
Dyes of formula—



(R^1 = subst. or unsubst. Alk; R^2 = acyl group of a carboxylic acid; L = subst. or unsubst. methin; n = 0 or 1; d = 0–2; Z = non-metallic atoms to complete a 5- or 6-membered ring) have photographic sensitising properties. C. O. C.

Aza Trinuclear Cyanine Dyes. General Aniline. *BP* 690,300

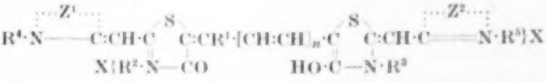
Dyes of formula—



(m = 0 or 1; n = 0–2; R^1 = H or, if desired when n = 1, C_1–C_2 Alk; R^2 and R^3 = same or different, subst. or unsubst. Alk, Ar, or aralkyl; R^4 = allyl or R^2; Z^1 and Z^2 = same or different residues of heterocyclic nuclei; X = acid radical; the carbocyclic rings of polycyclic derivatives may be further substituted) are obtained in excellent yield and purifiable state by treating a *cyclo*ammonium quaternary salt containing a reactive group in the 2- or 4-position with an azathiazolone cyanine dye in presence of a solvent and a basic condensing agent. C. O. C.

Unsymmetrical Tetranuclear Cyanine Dyes. General Aniline. *USP* 2,611,695

Dyes of formula—



(R^1 = H or, if n = 1, Alk; R^2 and R^3 = same or different Alk, allyl, Ar, or aralkyl; R^4 and R^5 = same or different aliphatic radical, Ar, or aralkyl; n = 0–2; X = acid radical; Z^1 and Z^2 = atoms to complete a heterocyclic nucleus, being the same when R^2 and R^3 are different, and different when R^2 and R^3 are the same) are photographic sensitisers which resist both displacement from the silver halide grains by colour formers and diffusion from one emulsion to another. C. O. C.

Preparing Organic Pigments in Finely Divided Form. General Aniline. *USP* 2,611,771

Forcing a solution of the pigment as a thin film or sheet into and wholly within a stationary or laminarly flowing body of an aqueous drowning liquor results in a product of finer and more uniform particle size than that prepared by conventional and spray methods of drowning. C. O. C.

Furnace Black. Phillips Petroleum Co. *BP* 689,134

Modification of the method of *BP* 621,031 (J.S.D.C., **65**, 418 (1949)) to obtain an increased yield and a tar-free product.

BP 689,141

A process for lowering the pH of furnace black and rendering it more hydrophilic. C. O. C.

Carbon Black. Phillips Petroleum Co. *USP* 2,608,470

Carbon black and diesel fuel are produced in high yield from a highly aromatic stock. C. O. C.

Ferric Hydroxide from Aniline Sludge. K. M. Nahas. *USP* 2,608,468

The sludge is brought to a 50% solids content with water, and then digested with acid to form a plastic mass of oxides or basic salts, less acid being used than would combine with the total amount of iron present. C. O. C.

Titanium Dioxide. Säurefabrik Schweizerhall. *BP* 689,123

A method of treating vaporised $TiCl_4$ at 600° c. in presence of air so that TiO_2 of at least 90% rutile content is produced. C. O. C.

Luminescent Zinc Sulphide Phosphors. General Electric Co. *USP* 2,610,154

A saturated solution containing ZnS and/or CdS and an activator, e.g. Cu or Ag, is heated at 250–374° c. until a product of homogeneous structure is obtained. To get the best results the raw materials before being dissolved should have a particle size ca. 200 Å., the finer the particle size the more complete the recrystallisation of the final material. C. O. C.

Fluorescent Effects on Textile Substrates (VIII p. 223).

V—PAINTS; ENAMELS; INKS

Viscosity of Pigment Dispersions [Printing Inks]. A. Voet and L. B. Suriani. *Amer. Ink Maker*, **30**, (5), 37–39, 67 (1952): *Chem. Abs.*, **47**, 3000 (25 March 1953).

Milori and Monastral Blues, Ba lithol resinated and unresinated, chrome yellow, Benzidine Yellow, channel black powder and pellets, and furnace black were dispersed, in various concentrations, in heat-bodied linseed oil, naphthenic mineral oil, limed rosin–mineral oil varnish, and maleic-modified rosin–diethylene glycol varnish. Measurement of viscosity (η) with a rotational viscometer gave the relation $U_R = e^{K\psi}$ (U_R = ratio of plastic viscosity of the dispersion to the vehicle viscosity;

ψ = ratio of pigment volume to vehicle volume; κ = a constant characteristic of the pigment–vehicle combination). C. O. C.

Electrophoresis of Pigments in Organic Solvents—III. H. Brintzinger, R. Haug, and G. Sachs. *Farbe und Lack*, **58**, 522 (1952): *Chem. Abs.*, **47**, 3001 (25 March 1953).

In non-polar solvents organic pigments containing sulpho groups are positively charged, but a nitro group, e.g. in Lake Red G, renders them negative. As sulphonated pigments are negative in water, their positive charge is thought to derive from the metal ions held by the undissolved azo pigment. Hansa Yellow 5G is negative in some polar solvents, but positive in others unless the adsorbed ions causing this "false charge" are removed by extracting the pigment for 40 hr. with water. Pairs of pigments with contrasting charges (Lithol Rubine BN–Hansa Yellow G, Heliogen Blue–Heliogen Green) in non-polar solvents go to the opposite poles during electrophoresis, but in polar solvents they form bridges between the electrodes and flocculate during sedimentation; with excess of one pigment precipitation occurs only at one electrode. Wetting agents, e.g. Basopal NA, prevent such flocculation. Inorganic pigments must be dried (for 8 hr. at 150–200°c. *in vacuo* over P_2O_5) to < 0·05% moisture to prevent bridge formation during electrophoresis in dry non-polar solvents, but organic pigments neither form bridges nor flocculate under these conditions, dried or not, even in fields of 20,000 v./cm. Small amounts (0·1%) of polar solvents act like water in causing bridging of anhydrous pigments in non-polar solvents; ethyl, butyl, and ammonium acetates, acetone, and nitrobenzene do not have this effect. Slightly dried and pressed (2–4000 atm.) pigments still bridge during electrophoresis unless more thoroughly dried. C. O. C.

PATENTS

Ink for Carbon Paper, Duplicating Machines, etc. J. R. Ehrlich. *USP* 2,610,921

Two dyes or pigments of different hues are used, one at least not being black. Both are insoluble in the vehicle used, the second being present in sufficient quantity either to produce together with the first pigment a different ink colour or to impose its own colour and completely suppress that of the first pigment. The second pigment must be susceptible to the action of certain chemicals which either destroy it completely or change its hue, whereas the hue of the first pigment must be unaffected by these chemicals. Thus by treating impressions made with the ink with the appropriate chemical the colour of the impressions can be changed. C. O. C.

Hardening of Resin Coatings on Metal. ICI. *BP* 689,833

Coatings of thermohardening resins on metal articles are hardened by immersing the coated article for a short time in hot water. C. O. C.

X-Ray Study of the Thermal Decomposition of Prussian Blue (IV p. 214).
Hiding Power of Pigments as a Function of their Particle Size (IV p. 214).
Ink Transfer to Representative Groups of Paper (XI p. 225).

VI—FIBRES; YARNS; FABRICS

The Great Adventure of Fibre Structure. W. T. Astbury. *J. Textile Inst.*, **44**, P 81–P 97 (March 1953).

The latest theories on the structure of proteins and synthetic polypeptides are discussed in the 1952 Mather Lecture, and a description is given of X-ray and electron-microscope studies on collagen and bacterial flagella. J. W. B.

Structure and Properties of Natural and Allied Fibres. W. R. Moore. J.S.D.C., **69**, 149–154 (May 1953).

Electrical Resistance Measurements on Fibres and Fibre Assemblies. S. P. Hersh and D. J. Montgomery. *Text. Research J.*, **22**, 805–818 (Dec. 1952).

The electrical resistance of fibres is measured because of the relation between this property and static electrification. Both natural and certain man-made fibres were investigated at R.H. of 52–85%, but the resistances of other synthetic fibres (Orlon, Dacron, dynel, polyethylene, Velon) were too high to be measured on the apparatus. A. B.

Partial Carboxymethylation of Cotton. G. C. Daul, R. M. Reinhardt, and J. D. Reid. *Text. Research J.*, **22**, 787–792 (Dec. 1952).

The action of chloroacetic acid on cotton in the presence of NaOH is studied. Time, temperature, and concentration are varied, and it is shown that small quantities of acid alter the properties of cotton considerably. This is possible in standard textile machinery, giving cloth with a crisp handle and a slightly starched feel. Tensile strength and elongation of treated cotton are increased, dyeing properties are changed, giving in general lower affinity than that of mercerised cotton, and soil resistance and soil removal are improved. A. B.

Sorption of Synthetic Surface-active Compounds by Textile Fibres. A. S. Weatherburn and C. H. Bayley. *Text. Research J.*, **22**, 797–804 (Dec. 1952).

The sorption of surface-active compounds from aqueous solution by cotton, viscose rayon, acetate rayon, nylon, and wool has been measured. In general, cationic compounds were absorbed to the greatest extent and non-ionic the least. The various fibres absorbed the agents in widely differing orders. A. B.

Breeding of Bast Fibre Plants for High Fibre Content. G. Bredemann. *Faserforsch. und Textiltech.*, **4**, 33–36 (Jan. 1953).

Breeding experiments on hemp (*Cannabis sativa* L.) have produced, over a period of 17 years, a two- to three-fold increase in the fibre content of the plant. A. E. S.

Air Flow Method of Measuring the Specific Surface of Jute. II—Chemically Treated Fibres. M. M. Roy. *J. Textile Inst.*, **44**, T 90–T 94 (March 1953).

Changes in stiffness and cross-sectional characteristics of jute fibres consequent upon different degrees of delignification by the chlorite method and upon treatments in 5 and 12·5% NaOH at 0°c., and the effects of such treatments on the proportionality factor in the Kozeny equation as used for deriving the specific volume by air permeability, are studied. Cross-sectional characteristics are unaffected by chemical treatment, but stiffness is considerably modified; as stiffness increases, so does the proportionality factor. 5% NaOH reduces stiffness by 50%, and 12·5% NaOH almost to that of cotton. J. W. B.

Association of Glucose, Arabinose, and Xylose in Jute. D. B. Das, M. K. Mitra, and J. F. Wareham. *Nature*, **171**, 613–614 (4 April 1953).

Selective hydrolysis of jute α-cellulose with formic acid is followed to obtain simple oligosaccharides and to identify by paper chromatography the gluco-xylose or gluco-arabinose linkages. After hydrolysis with 85% formic acid for 12 min. at 135°c., a chromatogram shows, in addition to spots of xylose, glucose, and arabinose, a prominent new spot, which disappears after a further 3 hr. hydrolysis, between the uronic acid and glucose spots. The new complex is probably a triose or a tetrose; after isolation, purification, and further hydrolysis, it appears on the chromatogram along with glucose, xylose, and arabinose. A chemical union between α-cellulose and pentosans is thus indicated—a simple oligosaccharide of glucose, arabinose, and xylose which has not previously been isolated, probably because arabinose is generally in the furanose form whereas in this instance the pyranose form is present. J. W. B.

Acidic Properties of Jute Fibres. W. G. Macmillan and B. P. S. Gupta. *J. Indian Chem. Soc.*, **29**, 737–746 (Oct. 1952).

The free acidity of jute fibre is due to the presence of a small amount of free uronic carboxyl groups, mostly combined with lignin by ester linkages. Reaction with NaOH yields acetic acid, mostly associated with the carbohydrate fraction. During hydrolysis a portion of uronic acid was eliminated, and the decrease in aldehyde content is attributed to a Cannizzaro reaction. Some oxidative changes also occur in the carbohydrate fraction. It is thought that a portion of lignin in jute is combined with the holocellulose fraction through a glucoside linkage. A. J.

Damage of Linen by Microbes. W. Wegener and R. Questel. *Melliand Textilber.*, **34**, 12–16 (Jan.); 100–102 (Feb.); 171–178 (March 1953).

A description of observations carried out over a period of 18 months on yarns and fabrics of known history. The qual. and quant. nature of the micro-organisms shaken off the material at intervals exhibits rhythmic variations. The mechanical properties of the linen at various stages of attack are investigated. The tensile strength–time curve is almost the mirror image of the pH–time curve. Damage caused by micro-organisms gives rise to a characteristic sudden increase in the elongation at break of linen and cotton yarns after 5 months. 24 Photomicrographs show degenerate forms on linen as substrate; 33 further photomicrographs illustrate microbe damage to linen and cotton. H. E. N.

Fractionation of Cellulose. E. J. Pagé. *Text. Research J.*, **23**, 28–33 (Jan. 1953).

Various celluloses have been examined for molecular weight heterogeneity both before and after exposure to the degradative effect of ultraviolet radiation. Significant changes in the molecular weight distribution patterns are recorded and discussed. A. B.

Vapour Sorption of Cellulose at High Relative Humidities. G. A. Richter, L. E. Herdle, and W. E. Wahtera. *Ind. Eng. Chem.*, **44**, 2883–2893 (Dec. 1952).

Extensive measurements have been made of the sorption of water and other vapours by cellulose. Several types of cellulose were used, and the effects of various pretreatments (e.g. drying, oxidation, hydrolysis) of the cellulose examined. Possible explanations of the results are suggested. B. M.

Effect of High-energy Cathode Rays on Cellulose. J. F. Saemen, M. A. Millett, and E. J. Lawton. *Ind. Eng. Chem.*, **44**, 2848–2852 (Dec. 1952).

Irradiation of cellulose with high-voltage cathode rays caused depolymerisation, reduction in crystallinity, and extensive decomposition at high dose levels. These effects occurred in both crystalline and non-crystalline regions. The rate of hydrolysis by dil. acid increased when the average chain length was < 200 glucose units. B. M.

Mechanism of the Absorption of Inhaled Carbon Disulphide, and its Location in the Human Body. H. Demus. *Faserforsch. und Textiltech.*, **4**, 22–33 (Jan. 1953).

An atmosphere containing CS_2, and the exhaled air, blood, and urine of persons working in this atmosphere, are analysed for CS_2 by a method depending on the conversion of the latter into potassium methyl xanthate, which may be estimated iodimetrically. The rate of absorption of CS_2 by the body is thus found as a function of the time and of the CS_2 content of the atmosphere. The CS_2 content of the blood becomes appreciable after ~ 10 min. exposure, but it falls rapidly after the person has been removed from the polluted atmosphere; for diagnosis purposes this estimation is of less value than tests carried out on the urine, where the effects are more persistent. Experiments in which the body is exposed to the polluted atmosphere, while the respiratory system is supplied with fresh air, indicate that only the lungs are concerned to an appreciable extent in the absorption of CS_2 by the body. A. E. S.

Fine Structure of Regenerated Cellulosic Fibres. E. Elöd and H. Rauch. *Melliand Textilber.*, **34**, 1–11 (Jan. 1953).

In this investigation topochemical acetylation, phase-contrast microscopy, and microscopy under oblique illumination are used. Topochemical acetylation consists in treatment of the dry fibre with e.g. a mixture of dry benzene (240 c.c.), acetic anhydride (60 c.c.), and H_2SO_4 (0·5 c.c.), liquor ratio 20 : 1, at 40° c. The triacetate formed can be removed e.g. with chloroform–methanol (9 : 1). In carrying out such acetylations for periods varying from 2 to 8 days, successive layers of the fibres can be removed ("peeling method"). The outermost layer of viscose rayon is thus shown to be denser than the core, whereas in cuprammonium rayon the core is denser, and in Lanusa (rayon staple) there is little difference between the outer region and the core. The results are discussed in connection with crease-resisting. 22 Photomicrographs. H. E. N.

Effect of the Degree of Polymerisation on the Serimetric Properties of Regenerated Cellulose Fibres. J. R. Coley. *Text. Research J.*, **23**, 34–36 (Jan. 1953).

The variation of the tensile strength of viscose rayon with the degree of polymerisation (D.P.) is investigated. The optimum D.P. is 375–425, above which there are no beneficial changes in the tensile properties of the fibres. A. B.

Treatment of Cellulose prior to Acetylation. C. J. Malm, K. T. Barkey, D. C. May, and E. B. Lefferts. *Ind. Eng. Chem.*, **44**, 2904–2909 (Dec. 1952).

Cellulose is treated with acetic acid and/or acetic acid–sulphuric acid mixtures prior to acetylation. The effect of variations in such treatment on the reactivity of cellulose is considered. High reactivity to acetylation is obtained when there is rapid and uniform sorption of sulphuric acid, the amount sorbed being less important than uniformity of distribution. Such uniformity is obtained if the cellulose is activated with acetic acid for a time depending on the history of the cellulose, its moisture content and that of the system, and the temperature. The principal function of the catalyst treatment is reduction of the cellulose chain length prior to acetylation. Chain length reduction depends on temperature, the amount of sulphuric acid sorbed, and the moisture content of the system. High cuprammonium viscosity values are obtained if the sulphuric acid is not evenly distributed. W. R. M.

New Method of Producing the Allwörden Reaction. E. H. Mercer and R. L. Golden. *Text. Research J.*, **23**, 43–44 (Jan. 1953).

The immersion of wool fibres in chlorine water causes the formation of bubbles or blisters on the surface, as discovered by Allwörden. This reaction is shown to occur also when wool is treated with peracetic acid and then with sodium bicarbonate solution. This new method is evidence of an entirely external epicuticle. A. B.

Stress Relaxation of Fibrous Materials. I—Instrumentation and Preliminary Results. E. T. Kubu. *Text. Research J.*, **22**, 765–777 (Dec. 1952).

Apparatus used in stress-relaxation measurements is described, incorporating ring-dynamometer strain gauges and linear variable differential transformers. Results are given for the effects of urea, hydrochloric acid, cysteine, thioglycollic acid, and sodium bisulphite on the stress-relaxation behaviour of wool keratin. The behaviour of wool, silk, and nylon in water is compared. A. B.

Stress Relaxation of Fibrous Materials. II—Kinetics of the Reduction of Wool Keratin by Cysteine. E. T. Kubu and D. J. Montgomery. *Text. Research J.*, **22**, 778–782 (Dec. 1952).

The kinetics of the reaction between cysteine in solution and cystine in keratin is discussed. The reaction is studied as a function of cysteine concentration, hydrogen ion concentration, and temperature by the stress-relaxation technique. A heat and an entropy of activation are determined, and their significance is discussed. A. B.

Apparent Degradation of Wool by Diazomethane Solutions. I. J. O'Donnell and J. M. Swan. *Nature*, **171**, 571 (28 March 1953).

Diazomethane, prepared from nitrosomethylurea, is added to wool over a period of several days, together with small quantities of water. The wool is extensively degraded, the product containing no sulphur, being almost completely soluble in water, and diffusing through Cellophane. During the reaction the wool looks as if it is being treated with strong alkali. The reason is that diazomethane contains methylamine as impurity: in presence of water this is methylated to give, finally, tetramethylammonium hydroxide in sufficient quantities to digest the wool. Other basic impurities may have a similar effect. Partial removal of methylamine is achieved by repeated treatment with either CH_3I or p-toluenesulphonyl chloride, followed by distillation, and the base-free solution does not degrade wet wool. It is suggested that caution is necessary in the use of diazomethane in protein studies, and also that previous work on the action of diazomethane on cotton may be in error because of contamination with tetramethylammonium hydroxide. J. W. B.

The α–β Transformation in Stretched Hair. A. Elliott. *Text. Research J.*, **22**, 783–786 (Dec. 1952).

Infrared spectra show that there is a mixture of α and β structures both in natural hair and in hair which has been extended 100%, and that the orientation of the β-material, at least, is very imperfect. It is therefore concluded that no simple relationship exists between the extension of the molecular chains on unfolding and the extension of the whole fibre. It is also considered that the amorphous as well as the crystalline regions should be considered in the interpretation of X-ray diffraction diagrams. A. B.

Formation of Fibres from Protein Monolayers. J. G. Kaplan and M. J. Fraser. *Nature*, **171**, 559–560 (28 March 1953).

If dilute solutions of ovalbumin at pH 2·25 are treated in a boiling water bath or with ultraviolet radiation and then spread in monolayers at pH 4·8, it is difficult or impossible to form fibres by compressing these films, and, if formed, the fibres are different from those obtained from monolayers of untreated ovalbumin. Similar results are given with egg albumin. Insulin and gliadin do not form fibres, and their films show expansion patterns similar to those of other proteins which have been irradiated. It is suggested that such modification deprives the molecule of two-dimensional specificity. J. W. B.

Polymerisation of 6-Hexanolactam. A. B. Meggy. *J.C.S.*, 796–798 (March 1953).

The polymerisation of 6-hexanolactam is of especial interest for the production of textile fibres, and it is now interpreted in terms of two equilibrium constants, viz. K_1, which determines the ratio of monomer to polymer at equilibrium, and K_2, the chain length of the polymer. From the change of K_1 and K_2 with temperature, the approximate values of ΔH and ΔS for the reactions involved can be calculated. The results are now used for calculation of the chain length of the polymer in equilibrium with liquid water at 220–280°c. H. H. H.

Kinetics of the Crystallisation of Hexamethylene-adipamide Polymer (6.6 Nylon). P. W. Allen. *Trans. Faraday Soc.*, **48**, 1178–1185 (Dec. 1952).

The rate of crystallisation of hexamethylene-adipamide polymer from the melt has been studied at 245–255°c. with melting temp. of 270–300°c. Results suggest that the process involves a nucleation mechanism. S-shaped crystallisation curves have been fitted to a rate equation, the derivation of which suggests that nuclei from which crystallites grow occur sporadically in time and space and that the volume of the crystallites increases linearly with time. The crystallisation curves show induction periods, which probably represent times required for nuclei to grow to a critical size. W. R. M.

Concentration–Viscosity Curves as an Index of the Cross-linking of Perlon. H. Sauer. *Faserforsch. und Textiltech.*, **4**, 14–21 (Jan. 1953).

Viscosity measurements are made on solutions in 96% H_2SO_4 of Perlon polymer taken at various stages of the fibre-manufacturing process and after certain laboratory treatments, e.g. exposure to oxygen while in contact with various glass and metal surfaces. The relation between specific viscosity η and concn. (c g. per 100 g. of solvent) is expressed in the form—

$$\eta = x(c + zc^2)$$

where x is a measure of the degree of polymerisation and z is a measure of the degree of cross-linking, envisaged here as a reversible process in a state of dynamic equilibrium. Oxidation processes lead to a fall in x and an increase in z, the latter being closely related to the extent of yellowing of the polymer. Under manufacturing conditions, the relatively insol. material formed in this way may become dispersed in the polymer in the form of small particles, which can give rise to weak nodular places in the filament and can affect its drafting properties. A. E. S.

Morphology of Chrysotile Asbestos Fibre. W. Noll and H. Kircher. *Naturwissenschaften*, **39**, 158–159 (1952): *Chem. Abs.*, **47**, 2566 (25 March 1953).

The spiral or wave appearance of chrysotile fibres is microscopic. The structure of the fibrils and capillaries is submicroscopic. C. O. C.

PATENTS

Filaments and Strings from Collagen. B. Braun, Melsungen. *BP* 689,582

Collagen filaments and strings, e.g. surgical stitching filaments or racket strings, are produced from animal tendons by disintegrating them into fibres while cooling with copious additions of water, the aqueous fibrous material being partly drained and then adjusted to pH 2·5–4·5. The highly swollen mass is, if necessary after further homogenisation, cast into films which can be cut into strips, which in turn are twisted into filaments. J. W. B.

Asbestos Dispersions. Raybestos-Manhattan. *BP* 689,692

Tightly bound aggregates or bundles of asbestos are treated with surface-active agents, which loosen the fibres and free them in a soft gelatinous mass, thus leading to a hitherto commercially unattainable yield of fibres with high length : diameter ratio. In one example rock asbestos of the Canadian chrysotile variety, in pieces about 2 in. × ¼ in. × ¼ in., is immersed in 15 times its wt. of 1% aq. sodium dioctyl sulphosuccinate at room temp. After a few days all the particles become softened and, apart from natural mineral impurities, remain as a gelatinous finely dispersed mass having strong colloidal properties. Some slight agitation and dilution lead to a suitable fibrous slurry. A list of suitable surface-active agents is included. J. W. B.

Cellulose Ester Fibres of Improved Recoverable Elasticity. BrC. *BP* 689,036

Fibres composed of $\ngtr$ 80% by weight of cellulose acetate and $\nless$ 20% of an *iso*cyanate- or *iso*thiocyanate-modified linear polyesteramide have much more recoverable extensibility than fibres consisting of cellulose acetate alone. C. O. C.

High-tenacity Rayon. Celanese Corpn. of America. *BP* 688,781

Variation in physical properties of high-tenacity rayon made by hydrolysis of cellulose acetate is prevented by reducing the amount of residual solvent to < 1% by wt. before stretching, e.g. by passing air through the loose material. W. G. C.

Water-soluble Multifilament Yarn of Hydroxyethyl Cellulose. Union Carbide & Carbon Corpn. *USP* 2,609,569

Yarns of dry tenacity > 0·7 g./denier and ultimate elongation 10–30% or more are obtained by wet-spinning an aq. soln. of a water-soluble hydroxyethyl cellulose preferably free from inorganic compounds. The hydroxyethyl cellulose used should, in 5% aq. soln., have a viscosity at 20°c of $\nless$ 1000 centipoises measured with a Hoeppler viscosimeter. The products are used as scaffolding threads. C. O. C.

Polyvinyl Alcohol Filaments. DuP. *USP* 2,610,359–60

Highly oriented, high-tenacity filaments resistant to boiling water are produced by polymerising vinyl formate or acetate in absence of water and stopping polymerisation (*a*) before the polymer forms 60% of the mixture, and (*b*) before > 75% of the monomer is converted; the polymer is then hydrolysed to polyvinyl alcohol, which is spun from aqueous solution, the filament being stretched to three times its length, washed, and dried; the dried filament is then stretched at 200–240°c to 2·5 times its previous oriented length. C. O. C.

Spinning Polyvinyl Chloride. Basf. *BP* 688,715

Filaments of polyvinyl chloride are obtained by spinning a solution in a water-soluble cyclic ether, e.g. tetrahydrofuran, into water or an aqueous solution, and leading the coagulating liquid in the same direction as the freshly spun filaments at such speed that the liquid imparts substantial stretch. W. G. C.

Solvents for Acrylic Polymers. BrC. *BP* 690,553

Nitroalkanols of 2 or 3 C, particularly 2-nitroethanol, are good solvents for producing spinning solutions of polyacrylonitrile or copolymers of acrylonitrile and other vinyl compounds. C. O. C.

Spinning Polyacrylonitrile Fibres. Industrial Rayon Corpn. *BP* 689,248

Polymers containing > 80% acrylonitrile are dissolved in a cyclic carbonate of a 1:2-, 2:3-, or 1:3-dihydric aliphatic alcohol having < 5 C atoms in its alkylene

radical, e.g. ethylene carbonate, and spun into a coagulating medium comprising a water-soluble polyalkylene ether glycol HO·A·[O·A]$_n$·OH (A = alkylene of 2–3 C; $n > 1$), e.g. tripropylene glycol. W. G. C.

Synthetic Fibres from Polymers and Copolymers of Acrylonitrile. American Cyanamid Co. *BP* 689,742

A soluble thermoplastic produced mainly from acrylonitrile is dissolved in conc. aq. calcium thiocyanate and extruded therefrom into water at −15 to +5°C., stretched 100% in presence of water at 70–110°C., a liquid composition containing an antistatic agent, e.g. 2% amidinourea octadecyl hydrogen sulphate, being applied, and continuously dried in a helical path.

BP 689,743

A soluble acrylonitrile polymerisation product containing ≮ 85% by wt. of combined acrylonitrile is extruded as above, stretched, cut into lengths while containing 13–75% of water, and dried while fully relaxed. The product has natural crimp.

BP 689,744

Polyacrylonitrile fibres produced as above are stretched, after coagulation, by being passed at a tangent between two rotating circular surfaces, whose different speeds maintain the fibres under tension and stretch them at least 100%. They are then dried by passing in a helical path over hot inclined rollers. J. W. B.

Coated Monofils and other Articles comprising Synthetic Linear Polyesters. ICI. *BP* 689,841

Articles, e.g. monofils, made of or coated with a synthetic linear polyester obtainable from a glycol HO·[CH$_2$]$_x$·OH (x = 2–10), terephthalic acid, and, if desired, one or more different dicarboxylic acids, are given improved flexure- and abrasion-resistant properties if they are coated with plasticised polyvinyl chloride. J. W. B.

Textile-like Materials from Organic High Polymers. B. Nilssen. *BP* 690,004

Highly polymerised organic substances are made plastic by means of heat, solvents, or plasticisers and are applied to rollers inlaid with grooves in a fine network pattern. Excess plastic is scraped off, and the inlaid material is transferred to a base, e.g. cellulose acetate film supported on a thicker fabric, from which it can be removed by dissolving the film base in a suitable solvent, thus leaving a patterned mesh of polymer. J. W. B.

Filaments of Large Cross-section produced from Several Finer Filaments. BrC. *BP* 689,040

The fine filaments are formed into a thread, which is led upwards in a straight line through a volatile liquid solvent. The straight path is continued on leaving the solvent until the thread is dry. This results in formation of a single coarse filament which has not been flattened by lateral pressure. C. O. C.

Xanthation of Cellulose. I—Reaction of Carbon Disulphide with Caustic Soda (III p. 209).
Effect of Preparatory Treatment on Chemical Composition of Flax (VII p. 222).
Reactivity of Protein Fibres—Some Analogies between Keratin and Collagen (XII p. 225).
Investigation of the Physical Structure of Synthetic Polyamides by means of Vibrational Spectra (XIII p. 227).
Experimental Investigation of the Molecular-weight Distribution Function of Polyamides (XIII p. 227).
Macromolecular Compounds. LII—Interaction of Polyester Molecules (XIII p. 227).

VII—DESIZING; SCOURING; CARBONISING; BLEACHING

Detergent Action. N. K. Adam and D. G. Stevenson. *Endeavour*, **12**, 25–32 (Jan. 1953).

Some modern work on the mechanisms of detergent action is described. Displacement of dirt of a greasy nature occurs by a rolling-up process, the detergent bringing about a drastic change in the angle of contact formed by the water–grease surface. The detergent also helps to disperse grease as an emulsion. Foaming is not a necessary condition of detergent action but may break oil up into droplets, assisting dispersal and mechanical removal of dirt. There is little evidence that solubilisation is important, except in detergent solutions more concentrated than are usually employed in washing. More dilute detergent solutions may cause dirt to swell and come off fibres in complex growths which are difficult to rinse away and may be redeposited. When fibres contain salt, droplets of water may be formed under oil adhering to the fibre and may grow by osmosis, possibly assisting detergent action by breaking up the oil. Rise in temperature normally assists detergent action by melting grease and increasing the solubility of the detergent. Adsorption is decreased as the temperature rises, and the dispersing power of the detergent may be decreased. W. R. M.

Modern Detergency. F. C. Harwood. *J. Textile Inst.*, **44**, P 105–P 113 (March 1953).

The nature of soiling, mechanism of detergency, and types of detergents are discussed from a launderer's viewpoint. J. W. B.

Distortion in Knit Fabrics and its Relation to Shrinkage in Laundering. H. M. Fletcher and S. H. Roberts. *Text. Research J.*, **23**, 37–42 (Jan. 1953).

The dimensional changes in laundering samples knitted from cotton, viscose rayon, acetate–viscose rayon, and nylon yarns have been measured in relation to changes in fabric structure. It is shown that changes in dimensions are due largely to a rearrangement of the fabric structure, and that the fabrics could be given a relaxation treatment so that the area would remain nearly constant on laundering. A. B.

Mobility of Oil Droplets, Interfacial Tension Measurements, and Gegenion Adsorption in Soap Solutions. B. D. Powell and A. E. Alexander. *Canadian J. Chem.*, **30**, 1044–1055 (Dec. 1952).

A microelectrophoretic technique has been used to determine the mobility of oil droplets in oil-in-water emulsions stabilised with sulphosuccinates NaSO$_3$·CH(COOX)·CH$_2$·COOX (X completes the diamyl, dihexyl, or dioctyl ester). The drop volume method was used to determine the interfacial tensions of the same systems; the experimental methods are fully described. The resulting curves showing the mobility of the Nujol droplets *versus* concn. of soap, and interfacial tension of different soap soln. against Nujol droplets *versus* concn., are discussed. It is shown how Henry's equation relating electrophoretic mobility and ζ potential may be applied to liquid droplets; the relationship between ζ potential and charge density is also discussed. Interfacial tension between Nujol droplets and soap soln. falls fairly rapidly as the soap concn. increases, until the micelle point is reached; thereafter it remains fairly constant, or passes through a shallow min. at the critical micellar concn. The factors governing these phenomena are discussed. Equations of state are given by means of which the fraction of gegenions bound may be calc., this latter decreasing slightly with increasing concn., but no explanation is offered. J. W. D.

Application of the Gibbs Equation to Charged Monolayers, and their Desorption from the Oil–Water Interface. J. T. Davies. *Trans. Faraday Soc.*, **48**, 1052–1061 (Nov. 1952).

The simple form of the Gibbs adsorption isotherm is shown to apply to dilute solutions of colloidal electrolytes in the presence of excess inorganic electrolyte. This is demonstrated theoretically from kinetic and electrical considerations and practically by measuring the rates of desorption of monolayers of cetyltrimethylammonium bromide from an oil–water interface. For these films the electrical potential is in good agreement with values derived from surface potential measurements and with the Gouy theory. The energy of adsorption of a CH$_2$ group at a paraffin oil–water interface is 811 g.cal. W. R. M.

Occurrence of Electrostatic Charges during the Manipulation of Anhydrous Solvents. M. Lecoustey. *Teintex*, **18**, 22–31 (Jan. 1953).

Fundamental concepts of static electricity are described, and it is explained why such charges may accumulate in industrial operations such as filtration, decantation, and dry-cleaning processes. Practical hints are given showing how electrostatic hazards can be reduced by means of suitable earthed conductor systems. G. L.

Sulphite Method of Bleaching Colour-woven Zephyrs. A. G. Tevfikov. *Tekstil. prom.*, **12**, 39 (Nov. 1952).

In a works bleaching process for zephyrs containing vat-dyed yarn, motes are removed by treatment in a horizontal kier (12–30 lb./sq. in. excess pressure, 4–5 hr.) in a solution of Na_2SO_3 (8–11 g./litre) and $NaHSO_3$ (3–4·5), the presence of the latter being necessary to prevent bleeding of dye. Kiering is preceded by rot-steeping and followed by washing, mercerising, and continuous hypochlorite treatment. A. E. S.

Effect of Preparatory Treatment on Chemical Composition of Flax. P. P. Viktorov. *Tekstil. prom.*, **12**, 36–38 (Oct. 1952).

Further discussion is given (see J.S.D.C., **67**, 164 (April 1951)) of the differences in behaviour during processing between green flax fibre and dew-retted flax. Comparative analyses show that the retted fibre has a somewhat higher content of wax and much lower contents of mineral matter, tannins, and pectins. Also, the "wax" extracted from retted fibre is found to have a less unsaturated character (I.V. of benzene extracts— 72·6 (dew-retted), 96·8 (green)), due, it is considered, to oxidation and polymerisation reactions during retting. Attempts are made to detect the presence of rubber formed in this way (see *loc. cit.*), but the results are negative. It is now considered unlikely that difference in the contents of wax and of unsaturated substances can account for the observed differences in behaviour. The Fe content increases during retting, and it is considered that Fe salts extracted from the grass and soil are fixed in the fibre by tannins and pectins, producing coloured substances, which are considered to account, in part, for the increased resistance to bleaching treatments. However, the main cause of the persistent grey colour of the retted flax is considered to be the presence of residues of micro-organism colonies, particularly of *Cladosporium herbarum*; some experimental evidence is given in support of this view. The rapid tendering of green fibre in bleaching is attributed mainly to the effect of chemical action at dislocations, observable under the microscope, which are produced in the fibre during its mechanical separation. Tendering may be enhanced by the catalytic effect of manganese— the Mn contents of flax before and after retting are found to be 40 and 10 p.p.m. respectively. A. E. S.

Rationalisation of the Technology of Linen Bleaching. Z. A. Veynberg. *Tekstil. prom.*, **12**, 34–36 (Dec. 1952).

It is considered that in the usual linen bleach, in which alkali boils alternate with hypochlorite treatments, the purification attained in the boils is too low, so that the process becomes largely dependent on unnecessarily vigorous, fibre-degrading hypochlorite treatments. Attention should therefore be directed to increasing the purification attained in the alkali boil and to reducing the severity of the hypochlorite treatment. Various properties of linen yarn (strength, cuprammonium viscosity, and content of various impurities) are determined at various stages of laboratory bleaches (liquor ratio 20 : 1), and it is shown that in presence of oxidation inhibitors (pyrogallol, sodium sulphite) a higher alkali concn. can be used in the boil with increased removal of impurities and without destruction or loss of cellulose. Under these conditions, a very mild intermediate hypochlorite is required. A. E. S.

Resistance of various Materials to Corrosion in Sodium Chlorite Solutions— III (I p. 209).
Foaming of Surface-active Agents (III p. 209).
Sorption of Synthetic Surface-active Compounds by Textile Fibres (VI p. 218).
Work Study in Bleaching, Dyeing, and Finishing (VIII below).
Microscopic Investigations of the Bleaching and Dyeing of Furs (XII p. 226).

VIII—DYEING

Work Study in Bleaching, Dyeing, and Finishing. H. Mitchell. *Dyer*, **109**, 465–467 (3 April 1953).

Joseph Dépierre. E. Justin-Mueller. *Teintex*, **18**, 96–101 (Feb. 1953).

A description of the records of J. Dépierre (1838–1910). He contributed widely to contemporary textile chemistry, and published a book on Dyeing and Printing in 1891. G. L.

Application of Ultrasonic Waves to Dyeing. P. Alexander and G. A. Meek. *Melliand Textilber.*, **34**, 57–59 (Jan.); 133 (Feb.); 214–216 (March 1953).

Claims that the rate and quality of dyeing can be improved by irradiation with high-intensity sound waves are investigated using 250 and 17·3 kc./sec. vibrations. Although the improvements claimed are confirmed, they are not specific, and it is shown that they can be produced by conventional methods of agitation of the dyebath or of the fabric. No evidence is found of reduced size of micelle of high-mol.wt. soluble dyes, but dyeing with disperse dyes is assisted, probably because of greater dispersion. H. E. N.

Physicochemical Properties of the Surface of Aqueous Solutions. III— Mechanical Behaviour of Surfaces of Micellar and Macromolecular Solutions. J. Sasaki and H. Kimizuka. *Bull. Chem. Soc. Japan*, **25**, 318–322 (Oct. 1952).

The surface viscosity and rigidity of the following aqueous soln. (concentrations in g./litre) are measured, using a torsion ring method, and the corresponding mechanical models deduced— saponin (0·1— Newtonian flow), saponin (0·25— Voigt element), polyvinyl alcohol (0·002— Maxwell model with Newtonian flow), polyvinyl alcohol (0·1— Maxwell model in series with Voigt element), Crystal Violet (0·001— non-Newtonian flow). A. J.

Diffusion across Interfaces. A. F. H. Ward and L. H. Brooks. *Trans. Faraday Soc.*, **48**, 1124–1136 (Dec. 1952).

A study of the diffusion of some aliphatic acids across a water–toluene interface without stirring. Concentrations immediately next to the interface in the two layers remained constant throughout diffusion with a ratio equal to the equilibrium distribution ratio. The passage of some substances of low solubility into solution in water under conditions of diffusion without stirring has also been studied. W. R. M.

One-dimensional Diffusion with the Diffusion Coefficient a Linear Function of Concentration. R. H. Stokes. *Trans. Faraday Soc.*, **48**, 887–892 (Oct. 1952).

Diffusion with a diffusion coefficient which is a linear function of concentration is discussed for one-dimensional diffusion from an initially sharp boundary between two semi-infinite columns of liquid. Numerical solutions are obtained for various degrees of concentration dependence, and methods are suggested for determining the diffusion coefficient and its dependence on concentration. W. R. M.

Exact Pattern of a Concentration-dependent Diffusion in a Semi-infinite Medium— II. H. Fujita. *Text. Research J.*, **22**, 823–827 (Dec. 1952).

A formal solution of the unidimensional diffusion equation $D(c) = D(0)/(1-\lambda c)^2$, where λ is an arbitrary constant. This gives a more rapid increase in D with concentration c than the form presented in Part I of this paper. (cf. J.S.D.C., **69**, 102 (March 1953)). A. B.

Method of Determining the Concentration Dependence of the Diffusion Coefficient. H. Fujita and A. Kishimoto. *Text. Research J.*, **23**, 59–63 (Jan. 1953).

A previous paper (cf. J.S.D.C., **68**, 280 (July 1952)) gave a method of determining the concentration dependence of the diffusion coefficient from experimental sorption data on the basis of the method of moments as applied to diffusion problems. The results given in the present paper do not assume the polynomial approximation in the analysis. A. B.

Interaction between Aniline Black and Cellulose. F. I. Sadov and G. K. Yurchenko. *Tekstil. prom.*, **12**, 35–36 (Oct. 1952).

Experiments on the formation of aniline black on various fibrous materials (cellulose, "monocarboxycellulose", "dialdehydocellulose", cellulose acetates, xylan, chitosan, wool, silk, Capron polyamide fibre) by the one-bath dyeing method and by the steaming method indicate that dyeing with formation of pigment that cannot be removed from the fibre by soaping at the boil or extraction with 80% acetic acid (in which the free pigment is readily soluble) occurs only when the fibre surface has a negative charge under the conditions of the oxidation reaction. Full fast blacks are obtained on cellulose, monocarboxycellulose, xylan, and silk; chitosan and cellulose diacetate give much

poorer results; and dialdehydocellulose, cellulose triacetate, Capron, and wool do not give fast dyeings. It is probable that the fastness of aniline black is determined by the forces between the negatively charged fibre and the basic dye molecules, but there are not sufficient data available to enable a final judgment to be made.
A. E. S.

Continuous Dyeing. F. Gund. *Melliand Textilber.*, **34**, 51–53 (Jan.); 130–132 (Feb. 1953).
A review of the continuous dyeing of vat and direct cotton dyes, including aftertreatment by diazotisation and development. The vat dyes are applied by pigment padding and steaming, and conditions, results, and faults are discussed. Direct cotton dyes are applied by padding and steaming. Recipes are given. H. E. N.

Modern Continuous Vat Dyeing. J. Müller. *Melliand Textilber.*, **34**, 134–136 (Feb.), 211–214 (March 1953); *Tex*, **12**, 150–157 (Feb. 1953).
A critical comparison of the processes used. The German contribution is emphasised. The special finely divided pigments are simpler to apply, but the vat-acid process gives speedier and more complete development and better penetration. Thickeners, particularly British Gum, are added to the pad-liquor to prevent migration and cover irregularities in rayons. Drying between padding and development is essential for rayons. Group I dyes are preferred. H. E. N.

Effects of the Soaping Aftertreatment on Vat Dyes. H. H. Sumner, T. Vickerstaff, and E. Waters. J.S.D.C., **69**, 181–194 (June 1953).

Resistance of Natural Indigo to Termites. A. Herfs. *Melliand Textilber.*, **34**, 50 (Jan. 1953).
It is shown that cotton dyed with natural or synthetic indigo is attacked by termites, the former being in no way more resistant. The method of application of either form does influence the speed and intensity of attack; e.g. the use of the $FeSO_4$ vat without souring has a distinct inhibiting effect. H. E. N.

Dyeing in the Carpet Trade. A. Gaunt and P. Robinson. J.S.D.C., **69**, 155–159 (May 1953).

Binding of Anions by Denatured Proteins. J. R. Colvin. *Canadian J. Chem.*, **30**, 973–984 (Dec. 1952).
The adsorption of eight anionic dyes by soluble and insoluble heat-denatured lysozyme has been determined at several temp. and pH values. The adsorption of methyl orange by seven other proteins, both soluble and heat-denatured, has also been studied as a function of temp. and pH; proteins examined include plasma albumin, β-lactoglobulin, ovalbumin, and pepsin. The isotherms are normal, reproducible, reversible, and independent of protein concn. Changes in adsorption brought about by denaturing are explicable only in terms of the disruption of a sheath of strongly orientated water molecules around small positive proteins. The solvation sheath that, under certain conditions, maintains a denatured protein in soln. also decreases its binding power for anions. The results indicate the importance of $-\Delta F$ of hydration in protein interaction studies; this is discussed at length. The pH dependence of adsorption of methyl orange and other anions by denatured proteins is normal, but $-\Delta H$ of adsorption per mole of anion bound is greater than for the corresponding native form, with which anion binding is almost insensitive to temperature. The current concept of unique specific binding sites on a protein, for weak interactions of this type, is discredited by the results of the investigation. J. W. D.

Silicon-containing Azo Dyes. IV—Dyeing Properties and Light Fastness. S. V. Sunthankar and H. Gilman. *Text. Research J.*, **23**, 53–58 (Jan. 1953).
The dyeing properties and the light fastness on cellulose acetate rayon of several azo dyes prepared from *m*-trimethylsilyl- and *m*-triphenylsilyl-*NN*-bis-β-hydroxyethylaniline have been examined. The dyes derived from the *m*-triphenylsilylaniline have been found to lack substantivity for cellulose acetate and to possess inferior light fastness, whereas the dyes from the trimethylsilyl analogue show fairly good substantivity and very good light fastness, the substantivity being less but the light fastness higher than for the corresponding *m*-methyl analogue. A. B.

Gas-fading of Dyed Goods. J. Eisele and W. Federkiel. *Melliand Textilber.*, **34**, 145–147 (Feb.); 224–225 (March 1953).
A review of the subject and of patents dealing with inhibitors and dyes fast to burnt gas fumes. H. E. N.

Fluorescent Effects on Textile Substrates. L. Wallner. *Teintex*, **18**, 69–93 (Feb. 1953).
The fundamental physics and present knowledge of the relationship between fluorescence and chemical constitution are summarised. Only a limited number of organic dyes exhibit strong fluorescence in daylight. The most numerous examples are found amongst the basic dyes, but valuable representatives exist amongst the acid, direct cotton, vat, and disperse types. Best effects have been obtained on acetate rayon and nylon staple. Methods of application for the dyeing of wool, silk, cotton, rayons, and nylon are given, and reference is made to recent developments and patents. G. L.

PATENT

Fur Dyeing. P. Poser. *BP* 689,800
Modification of *BP* 647,101 (J.S.D.C., **67**, 121 (1951)). Dyeing time is reduced by forcing the liquor along the surface of the skins in two opposite directions. Drying is accelerated by forcing air under pressure along the surface of the skins after the liquor has been drained off; this procedure may be replaced by or alternated with reduction of the pressure in the container, so as to facilitate evaporation of residual liquor left in the skins. C. O. C.

Synthesis of Water-repellent Dyes (IV p. 212).
Microscopic Investigations of the Bleaching and Dyeing of Furs (XII p. 226).
Pigmented Silicone Elastomers (XIII p. 227).

IX—PRINTING

Anthrasol Blue IBC in Printing. G. Torinus. *Melliand Textilber.*, **34**, 209–210 (March 1953).

Colour Development. V—Behaviour of Colour Developers towards Binder-free Silver Salts. K. Meyer, W. Brune, and H. Siebenlist. *Z. wiss. Phot.*, **47**, 129–136 (1952); **VI—Oxidation of Colour Developers by Emulsion Silver Bromide in Absence of Colour Couplers.** W. Brune and U. Kronacher. *Ibid.*, 137–144: *Chem. Abs.*, **47**, 2069 (10 March 1953).
V—The amounts of *NN*-diethyl-*p*-phenylenediamine (I) and sulphite used up in the reaction of colour developer solutions with ammoniacal Ag soln. and freshly pptd. AgBr were determined. The initial proportions of I, Na_2SO_3, and NH_2OH in the four solutions used were 1 : 2 : 0, 1 : 3 : 0, 1 : 1 : 2, and 1 : 2 : 4. The ratio of I to sulphite used up was 1 : 1 in solutions containing no NH_2OH. Addition of $CuSO_4$ did not change the ratio, and the initial ratio of I to oxidising agent is unimportant. The amount of Ag formed indicated that the I-sulphonate formed itself reduced the $Ag(NH_3)_2^+$ ion and binder-free AgBr. In presence of NH_2OH more sulphite is consumed per mol. of I, indicating that the NH_2OH–sulphite complex is oxidised by the Ag salt.
VI—The amounts of silver formed, and of I and sulphite used up, when precipitated AgBr and AgBr in a photographic emulsion are reduced, were determined. The developer solutions contained—(A) I (3 g.), Na_2SO_3 (2·5), K_2CO_3 (50), and water (1000); and (B) same as (A) with addition of NH_2OH sulphate (1), KBr (1), and Ca-sequestering agent (2). The initial ratio of I to AgBr was 1 : 0·59. With solution A and exposed emulsion 1 mol. of I and 1 mol. of sulphite were used up for 2 Ag formed. With soln. B the amount of Ag formed was 0·2–0·3 atom higher, probably because of development by NH_2OH. The ratio of I used up to Ag formed in presence of binder-free AgBr depended upon the initial ratio of I to AgBr; when the latter is 1 : 0·22, 1·2 Ag is formed by 1 mol. of I used up in soln A; when it is 1 : 4·16, 2·4 Ag is formed. The greater quantity of Ag was probably due to added reaction by I-sulphonate. When soln. B was used, even larger relative amounts of silver were formed. C. O. C.

PATENTS

Vat Dye Photoprints. General Aniline. *USP* 2,611,701
Excellent prints on a light background of high contrast and intensity can be obtained by treating a base carrying

a Prussian Blue image with a sulphenic ester of a leuco vat dye and an oxidising agent and causing image-wise oxidation of the leuco ester by the catalytic effect of the Prussian Blue. The Prussian Blue and unoxidised ester are then removed by alkali, leaving the vat dye image on the base. C. O. C.

Applying Colour to Printed Sheets such as Ceramic Transfers. J. A. Johnson. *BP* 690,428

The powdered colour is fed on to the sheet, previously coated with an adhesive in the pattern areas, which is then carried beneath rubbing pads mounted on bars bearing resilient insets of rubber, reciprocating movement being imparted to the pads through these insets. Uniform deposition of the colour over the pattern area is obtained. C. O. C.

Ceramic Transfers. Brittains. *BP* 690,623

An improved transfer paper for use in printing with ceramic colours comprises a decalcomania paper, e.g. a duplex or simplex paper, whose gummed side is joined by a water-soluble adhesive to a coating of a thermoplastic material which can be printed with ceramic colours and fluxes, becomes soft and adhesive at 50–100°C., and is volatilised or decomposed without residue below the maturing temperature of the colours and fluxes printed on it. C. O. C.

Colour Photography. ICI. *BP* 690,399

Modification of *BP* 651,059 (J.S.D.C., **67**, 250 (1951)). The stability of the aqueous solution of the anil is improved and its high rate of reaction with residual colour former maintained longer if the solution contains excess of either the aldehyde or the amino component of the anil. Attainment of full tinctorial strength of the masking image may sometimes be facilitated by aftertreatment with a substance which liberates the aldehyde from the anil. C. O. C.

Quantitative Study of Formation of Blue Dye in Colour Development (IV p. 212).

X—SIZING AND FINISHING

Some Aspects of the Drying and Heating of Textiles. VIII—Note on Modifications produced by Thermal Treatments of Acetate Rayon Fibres. J. M. Preston and M. V. Nimkar. J.S.D.C., **69**, 201–202 (June 1953).

Migration of Dyes or Resins during the Drying of Fabrics. H. Haas. *Melliand Textilber.*, **34**, 67–68 (Jan); 139–140 (Feb. 1953).

Results of experiments on the drying of wood are applied to a consideration of the migration of substances without affinity for the fibre during the drying of fabrics by convection. The process can be divided into three stages—(1) warming the fabric to a certain temp., (2) evaporation from the surface at approx. const. rate and temp., and (3) internal evaporation of water, the temp. rising again and the rate of drying falling. The temp. of the drying air has only a slight effect on migration. With increased air speed, relatively less water is lost during (2) and more during (3), less migration resulting. Lower humidity of the air also lessens migration. Infrared and cylinder driers cause pronounced migration towards the heated surface. High-frequency drying and drying at room temp. avoid migration, but are uneconomic. H. E. N.

Improvement of Lustre of Cotton. II—Decrystallising and Mercerising—Influence on Lustre. L. Fourt and P. Streicher. *Text. Research J.*, **23**, 23–28 (Jan. 1953).

Treatments in both anhydrous ethylamine and solutions of sodium hydroxide are shown to affect the lustre of cotton yarns in the same direction, although the effect is generally less for ethylamine. If the yarn is held under tension, an increase in lustre is obtained, but relaxed treatment decreases the lustre. After ethylamine treatment the portion of the cellulose which remains crystalline is still native cellulose, whereas after NaOH mercerisation the cellulose is more or less completely converted to hydrate cellulose. Measures of accessibility do not indicate changes in lustre primarily, but only indirectly. A. B.

Crease-resistant Cloth from Partly Carboxymethylated Cotton. G. C. Daul, R. M. Reinhardt, and J. D. Reid. *Text. Research J.*, **22**, 792–797 (Dec. 1952).

A method of applying resins to the acid form of partly carboxymethylated cotton cloth to produce crease resistance is described. The acid acts as a catalyst for the process, and the higher swellability of the modified cotton allows easier penetration of the resin-formers. A. B.

Milling of Fabrics containing Rayon Staple. H. Nuding. *Melliand Textilber.*, **34**, 218–219 (March 1953).

Milling in acid soln. at pH 3–4 and 25–50°C., with 120–150% moisture content and using mineral oil containing emulsifying agents, is preferred, because the process is cheaper, the rayon swells much less, and the dyed material remains brighter. H. E. N.

PATENTS

Crimping Fibres. Alexander Smith & Sons Carpet Co. *BP* 690,063

Permanent artificial crimp is imparted to textile fibres, in particular to wool, by gripping the fibres between closely spaced conveyor surfaces discharging into a zone where they are held compactly against fibres already there under pressure, the pressure being so arranged that the fibres are progressively crimped as they are delivered from the conveyor surfaces. The fibres are passed to a second zone, where they are treated under uniform conditions with suitable setting agents, e.g. pressure steam, or thioglycollic acid and its salts. J. W. B.

Yarn Conditioning. R. Mellor and S. Cheetham. *BP* 689,624

Yarn is conditioned by applying a dilute solution of a wetting agent, the quantity of agent being controlled by passing it and water through a proportional pumping apparatus in which the master piston is acted on by water under pressure and is provided with a movable stop to adjust the stroke. The master piston is coupled to one or more secondary pistons, which pump a solution of wetting agent to an outlet, where it joins the water expelled by the master piston, the mixture being ejected on to the material. J. W. B.

Imparting Crease- and Shrink-resistance to Cellulosic Textiles. L. Beer. *BP* 689,102

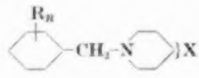
Textiles containing $\nless$ 50% of natural or regenerated cellulose and $\ngtr$ 50% of cellulose acetate are rendered crease-resistant and shrink-resistant on boiling by treating them with an aq. soln. containing 1-hydroxymethyl-5:5-dimethylhydantoin or dimethylhydantoin-formaldehyde (1–7% by wt.), bishydroxymethylurea, and a non-volatile water-soluble acid at pH 2·0–2·5, drying at 180–240°F., and then baking at 212–310°F. C. O. C.

Tracing Cloth, Holland Cloth, Measuring Tapes, etc. Monsanto. *BP* 689,381

Woven cotton cloth is coated and/or impregnated with a solution containing a copolymer of a *sec.*-alkyl hydrogen ethylene-$\alpha\beta$-dicarboxylate with a compound of formula R·CH:CH$_2$ (R = subst. or unsubst. phenyl) and an organic solvent for the copolymer, dried, and finally hot-calendered. Preferably the solution contains also polyvinyl butyral, with or without a compound capable of cross-linking the carboxyl groups of the copolymer. This gives a clear coating which is particularly suitable as a base for a photographic emulsion. C. O. C.

Mildewproof Cellulose produced by Reaction with Quaternary Chlorobenzylammonium Salts. Institute of Textile Technology, Charlottesville, Va. *USP* 2,609,270

Cellulose is rendered mildewproof by treatment with compounds of formula—



(R = Br or Cl; n = 1–5, X = a negative ion). They are applied from aqueous solution, if desired in presence of alkali, dried, and baked at 100–200°C. The proof resists washing. C. O. C.

Reducing the Felting Properties of Wool. American Cyanamid Co. *USP* 2,609,307

Treatment of the wool, if desired in presence of cellulosic fibres, with an aqueous colloidal solution of a polymerised cationic aminotriazine–aldehyde condensate containing an acid is followed by ordinary drying, which insolubilises the condensate without baking. C. O. C.

Permanent Sizing. General Aniline. *USP* 2,609,350

Textiles, particularly those of vegetable origin, are sized fast to washing by impregnating them with a mixture of a polyhydric alcohol and a synthetic resin obtained from maleic anhydride and a ring compound containing a single >CH:CH$_2$ group, and then baking to effect a cross-linking esterification action to set the finish in the fibre. C. O. C.

Laminated Fabrics. Celanese Corpn. of America. *BP* 688,961

Porous laminated fabric, suitable e.g. for collars, is obtained by bonding together two or more non-thermoplastic fabrics, at least one of which carries on the surface to be united discrete particles of a thermoplastic derivative of cellulose. Bonding is effected by pressure and heat in presence of a plasticiser and a volatile liquid which is a non-solvent for the adhesive at ordinary temperatures but which assists the coalescence of its particles at the temperature of pressing. C. O. C.

Synthesis of Water-repellent Dyes (IV p. 212).
Fluorescent Brightening Agents for use in Dry-cleaning Solvents (IV p. 216).
Partial Carboxymethylation of Cotton (VI p. 218).
Work Study in Bleaching, Dyeing, and Finishing (VIII p. 222).
Resistance of Natural Indigo to Termites (VIII p. 223).

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Ink Transfer to Representative Groups of Paper. I. Olsson and L. Pihl. *Svensk Papperstidning*, **56**, 197–201 (31 March 1953).

A study of the distribution of ink between paper and forme in the printing of glassine, Cellophane, supercalendered paper, and coated paper showed that increasing printing pressure increased the ink transfer between forme and paper; increasing amount of ink on the forme increased ink transfer up to a maximum; and increasing printing speed and viscosity of the ink decreased the ink transfer number. Through lack of sensitivity in the experimental set-up, no clear significant interaction was found between any of the independent variables. Supercalendered paper showed a more favourable ink transfer than glassine and Cellophane. For the latter two papers, a correlation was found between printing pressure and printing speed. S. V. S.

Existence of Branched Celluloses—Comparative Viscosimetry of Cellulose and Starch Solutions. A. J. A. van der Wyk and J. Schmorak. *Helv. Chim. Acta*, **36**, 385–397 (March 1953).

A comparison of the viscosimetric curves—(ln η_r)/c as a function of c—for vegetable, bacterial, and animal celluloses, with those for amylose, amylopectin, and glycogen, and also for the respective esters, indicates analogy between vegetable cellulose and amylose (also with cateniform carbohydrates), and between bacterial cellulose and amylopectin, pointing to a branched structure for the bacterial variety. Animal cellulose is highly ramified, and its curves are similar to those for glycogen. The bonds forming the branches are fragile and their presence is readily established. H. H. H.

Fractionation of Cellulose Acetate and Distribution of Non-cellulosic Compounds between the Fractions. T. Matsuzaki, S. Fukuhara, A. Hatano, and H. Sobue. *Bull. Chem. Soc. Japan*, **25**, 407–411 (Dec. 1952).

Cellulose acetates from cotton linters, Rayaceta, and a wood pulp were fractionally pptd. from acetone soln. by ethanol, and the viscosity of the fractions in acetone and cupriethylenediamine and the pentosan content were measured. There is a close relationship between acetone solubility and pentosan content. The initial and final fractions are not completely sol. in acetone and have a pentosan content > 0·04%. Acetone-sol. fractions have a pentosan content < 0·02%. The incompletely sol. fractions have low viscosity in cupriethylenediamine and probably low degree of polymerisation (D.P.), particularly with wood pulp acetate. The D.P. distribution of wood pulp acetates is probably more heterogeneous than that of those from cotton linters. A. J.

Carboxymethyl Cellulose. R. N. Hader, W. F. Waldeck, and F. W. Smith. *Ind. Eng. Chem.*, **44**, 2803–2812 (Dec. 1952).

A review of the commercial uses of carboxymethyl cellulose. Manufacturing processes are discussed, and a continuous process is described. B. M.

PATENTS

Paper or Paper Pulp. Defibrator A.B. *BP* 689,278

A method of producing pulp free from visible specks, from pulp furnish containing a bituminous material or wax as an impurity, includes thickening dilute pulp furnish to ≮ 35% consistency, heating it at ≮ 50 lb./sq. in. and 300°F., and defibrating the heated pulp so as to disperse the particles of impurities. S. V. S.

Calendering Mineral-coated Paper. Gardner Board & Carton Co. *USP* 2,611,717

A slippery, gelled solution of starch can be used in the ordinary calender box against the mineral-coated surface, where the adhesive for the mineral coating is a water-soluble starch, without causing stickiness of the coated surface and without any deleterious effect, provided that the strength of the starch solution is 4·5–15·0%. C. O. C.

Improving the Resistance to Soiling of Light-sensitive Photocopying Material. Ozalid Co. *BP* 690,433

The active side of the material is coated with a thin, elastic, waterproof, transparent or translucent film of a thermoplastic. The thermoplastic is first melted, and spread, e.g. by rollers, over the light-sensitive surface, which is then chilled. C. O. C.

Fractionation of Cellulose (VI p. 219).

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Reactivity of Protein Fibres—Some Analogies between Keratin and Collagen. J. B. Speakman. *J. Soc. Leather Trades Chem.*, **37**, 37–53 (Feb. 1953).

Wool and collagen contain similar proportions of basic amino acids, whilst the higher dicarboxylic acid content of the former is offset by the greater proportion of amide nitrogen in the latter. Swelling of wool with acids is less than that of collagen, being restrained by the cystine cross-linkages; these latter also complicate the titration of wool with alkalis. The wide divergence amongst titration curves obtained from the interaction of wool with a variety of acids is less when NaCl is present to suppress swelling, but this is not always practicable, e.g. with acetic acid. Importance of the swelling effect, and a method for calculating pH within the fibre, are illustrated in terms of the Donnan theory of membrane equilibrium; a "true" titration curve obtains when these factors are taken into account. Extension of these principles should reveal the essential similarity of different types of collagen in reaction with widely different acids. Differences in chain configuration may lead to differences in degree of hydrogen bonding between keratin and collagen, but they should react similarly with compounds which cause hydrogen bond breakdown; the effect of neutral salts such as KCl which have this action (and which also cause salt linkage breakdown) is discussed in connection with keratin and is of interest since such salts are important in leather manufacture. The small hydrothermal stability of collagen compared with that of keratin is attributed to the absence of cystine linkages between chains. The measurement of internal cohesion by determination of softening temperature is discussed. The rôle of cross-linking in tanning is still in dispute, but a discussion of the evidence that cross-linking does occur in keratin with formaldehyde, benzoquinone, and basic chromic acetate suggests strongly that

it takes place also with collagen. Steric factors such as the extent to which a protein structure is accessible to a reagent, and the distance between groups to be bridged, are of fundamental importance in tanning, and are even more pronounced with keratin when cross-linking is considered, since there is much less swelling than with collagen. The effect of the proportion of orientation to disorder on fibre properties, and methods for its determination, are considered. Difficulties in cross-linking arising from separation of the groups to be bridged may be overcome, in collagen, by the use of polyfunctional compounds such as lignosulphonic acid, but with keratin, where swelling is small, the fibre may be impregnated with a monomer such as methacrylic acid, which is then polymerised *in situ*. Cross-linking results if a monomer with a reactive side-chain is used, and it is suggested that such a procedure might be used for the controlled modification of the properties of collagen. J. W. D.

Conversion of Collagen to Gelatin and their Molecular Structures. W. M. Ames. *J. Sci. Food Agric.*, **3**, 454 (1952): *J. Soc. Leather Trades Chem.*, **37**, 103 (March 1953).

A systematic account of the conversion of collagen to gelatin. It is shown that collagen can be converted into two types of gelatin of differing nitrogen content. A study of heat degradation has made it possible to separate the effects of heat and chemical treatment in the preparation of one type. The results have been collated by means of diagrams of molecular structure, which lead to useful deductions and suggestions for further investigation. C. J. W. H.

Use of Mucolytic Enzymes in Unhairing Skins. D. Burton, R. Reed, and F. O. Flint. *J. Soc. Leather Trades Chem.*, **37**, 82–87 (March 1953).

Hides and skins are dehaired by treating with mucolytic enzymes, e.g. pectinase, which dissolve the mucoids responsible for much of the cohesion between hair and skin. As the operative pH values are much lower than those in lime processes, there is less damage to the pelt, which has improved appearance and handle. J. W. B.

Anion Activity–Cation Activity. New Idea for the Technology of Leather Manufacture. R. Schubert. *Leder*, **3**, 155 (1952): *J. Amer. Leather Chem. Assocn.*, **48**, 115–116 (Feb. 1953).

In tanning, dyeing, and fat-liquoring only complicated macromolecular compounds are used. The active group may be either anionic or cationic. Anionic and cationic dyes and anionic fat-liquors have long been used, but cationic fat-liquors are relatively new. Dyes should be designated as *anionic* or *cationic*, not as "acid" or "basic". Hide protein is amphoteric. It may bind anions and take a negative charge, or cations and take a positive charge. The power of hides to take up ions is limited. If the materials used in tanning, dyeing, and fat-liquoring all have the same kind of charge, the last ones used are taken up very slowly, whereas a material of opposite charge is taken up rapidly. The charges of various tannery materials and the effect of one on the absorption of another are discussed. C. J. W. H.

Colour of Leather and of Tanning Extracts. G. A. Bravo and T. Sola. *Congress of Italian Leather Chem. Assocn.* (May–June 1952): *J. Soc. Leather Trades Chem.*, **37**, 104–105 (March 1953).

The colour of leather is not directly related to the colour of the extract by which it is tanned, but is affected by its pretannage history as well as by the presence of acids and salts in the tanning liquor. Results obtained with the Tintometer are given. Colour readings vary with the illumination employed; even daylight under different conditions gives different results. C. J. W. H.

Rubbing Fastness of Suède Leather. R. C. Jurney and C. H. Geister. *J. Amer. Leather Chem. Assocn.*, **47**, 759–765 (Dec. 1952).

The fastness to rubbing of buffed and unbuffed goatskin chrome-tanned for suède and dyed with eight leather dyes is measured. Unbuffed samples have a fastness rating of 3–4, and buffed samples 1–2. Washing buffed samples with xylene removes particles of abraded leather ranging from 1 to 12 μ. It is concluded that crocking is largely due to these particles. A. J.

Microscopic Investigations of the Bleaching and Dyeing of Furs. F. Stather. *Ges. Abh. dtsch. Lederinst.*, (8), 3 (1952): *J. Soc. Leather Trades Chem.*, **37**, 35 (Jan. 1953).

Nineteen photomicrographs show the effect on the structure of rabbit hair of alkali treatment, carrotting, and dyeing. C. J. W. H.

Use of Atomic Models in Investigating Stable Configuration of Protein Chains. C. Robinson and E. J. Ambrose. *Trans. Faraday Soc.*, **48**, 854–869 (Sept. 1952).

Models of polypeptide chain folds have been built and examined, using the Hartley–Robinson atomic models (p. 227). Particular attention has been paid to properties of folds needed for correlation with polarised infrared data and with dynamic properties involved in the $\alpha \rightleftharpoons \beta$ transformation and in secondary folding. The possibility of the folds studied corresponding to those occurring in proteins or synthetic polypetides has been considered in the light of criteria proposed by other workers and of new criteria, these latter involving hydrogen bonding and restricted rotation about single bonds in the polypeptide chain. The 2_{7b} seven-membered ring fold and the N_{13} helix of Pauling, Corey, and Branson were most in accordance with these criteria, though, with respect to dynamic properties, the N_{13} helix appeared to have certain disadvantages. W. R. M.

Peptides. IV—Selective Removal of the *C*-Terminal Residue as a Thiohydantoin. Use of Diphenyl Phosphoro*iso*thiocyanatidate. G. W. Kenner, H. G. Khorana, and R. J. Stedman. *J.C.S.*, 673–678 (Feb. 1953).

Diphenyl phosphoro*iso*thiocyanatidate $(C_6H_5 \cdot O)_2PO \cdot NCS$ is conveniently prepared from diphenyl phosphorochloridate (chlorophosphonate) and potassium thiocyanate. In acetonitrile or dimethylformamide solution it gives 1-acyl-2-thiohydantoins in high yield from the triethylamine salts of *N*-acylated peptides; these are readily hydrolysed by alkali to a thiohydantoin and the acylated peptide or amino acid lacking the terminal residue. H. H. H.

Glycine Peptides. I—Polymerisation of Piperazine-2:5-dione at 180°c. A. B. Meggy. *J.C.S.*, 851–855 (March 1953).

The polymer of glycine which is formed when piperazine-2:5-dione is heated with water at 180°c. appears to exist in equilibrium with the dione in solution, but the equilibrium is continuously disturbed by hydrolysis and decomposition of the dione. For the reaction piperazinedione (solid) $\rightarrow$ polymer (solid), $\Delta F = -260$ g.cal. H. H. H.

PATENT

Chrome- and Salt-resisting Tanning Oils. Böhme Fettchemie. *BP* 689,724

Sulphonated tanning oils are rendered resistant to chrome and salt by addition of a water-soluble derivative of a polyalkylene oxide wax of mol. wt. $\nless$ 2000 and containing at least one aliphatic, alicyclic, aromatic, aliphatic–alicyclic, alicyclic–aromatic, or aliphatic–aromatic radical joined to the polyalkylene oxide wax through O, S, or N. C. O. C.

XIII—RUBBER; RESINS; PLASTICS

Seventh Soviet Conference on the Chemistry and Physical Chemistry of Macromolecular Compounds. *Izvestiya Akad. Nauk S.S.S.R. Otdel. khim. nauk*, 1134–1137 (Nov.–Dec. 1952).

The conference is noticed briefly. It approved a new, rational nomenclature for macromolecular compounds—The parent repeating unit of the macromolecule is enclosed in parentheses; if there are substituents, they are indicated by prefixes, and the expression is placed in brackets; finally, "poly" is prefixed to the bracketed or parenthesised expression. Thus polythene is poly(methylene), natural rubber is poly[2-methyl(butenylene)], and polyvinyl chloride and polyvinylidene chloride become poly[chloro(ethylene)] and poly[1:1-dichloro(ethylene)] respectively. The treatment of copolymers is exemplified by the name given to Vinyon—poly[75 chloro(ethylene) 25 acetoxy(ethylene)]. A. E. S.

New Type of Space-filling Atomic Models. G. S. Hartley and C. Robinson. *Trans. Faraday Soc.*, **48**, 847–853 (Sept. 1952).

An elaboration of the Stuart type of atomic models has been designed with a view to studying folding and flexural characteristics of high-polymer molecules. High tensile strength of links and free rotation about single links are obtained. Calculations of constructional dimensions are given. W. R. M.

Long-range Forces between Large Chain Molecules. C. A. Coulson and P. L. Davies. *Trans. Faraday Soc.*, **48**, 777–789 (Sept. 1952).

A study of dispersion forces between extended conjugated molecules and the way in which the dispersion energy varies when one molecule is displaced relatively to the other. W. R. M.

Chelate Ion-exchange Resins. H. P. Gregor, M. Taifer, L. Citarel, and E. I. Becker. *Ind. Eng. Chem.*, **44**, 2834–2839 (Dec. 1952).

Bivalent metal ions are adsorbed to different extents at different pH values on a *m*-phenylenediglycine resin, and separations can be effected. The reactions between metal ions and the resin were completely reversible. The nature of the complex formed is not known. B. M.

Investigation of the Physical Structure of Synthetic Polyamides by means of Vibrational Spectra. N. V. Mikhaylov, D. N. Shigorin, and S. P. Makaryeva. *Doklady Akad. Nauk S.S.S.R.*, **87**, 1009–1012 (21 Dec. 1952).

Vibrational bands in the infrared absorption spectrum associated with the N–H linkage are investigated for a soln. of ε-caprolactam in CCl_4 and for films of polycaprolactam formed in various ways and subjected to various aftertreatments. In ε-caprolactam the N–H links are modified by hydrogen-bonding, and two fundamental bands are found corresponding respectively to (*a*) the stronger bonding present in the cyclic double molecules and (*b*) the weaker bonding present when association occurs with chain formation. In the polymers, also, the same bands can be distinguished; they now represent two types of interchain NH···OC linkages and are found at (*a*) 3250 cm.$^{-1}$ (overtone, 6380 cm.$^{-1}$) and (*b*) 3400–3450 cm.$^{-1}$ (overtone, 6380 cm.$^{-1}$). In addition, there is a band at 3080 cm.$^{-1}$ (overtone, 6090 cm.$^{-1}$), considered to be associated with still stronger, *intra*chain hydrogen bonds, the formation of which leads to folding of the chain. Swelling of the polyamide film in 1% H_2SO_4 results in a decrease (to about one-third) in the ratio of inter- to intrachain linkage, while heating of the film at 170°c. *in vacuo* for 7 hr. results in an increase ($\sim$ twofold) in this ratio. A. E. S.

Experimental Investigation of the Molecular-weight Distribution Function of Polyamides. S. E. Bresler, V. V. Korshak, S. A. Pavlova, and P. A. Finogenov. *Doklady Akad. Nauk S.S.S.R.*, **87**, 961–964 (21 Dec. 1952).

Polyamides are formed by reaction in methanol soln. (no experimental details), and the solutions are fractionated. For each fraction the sedimentation const. and the diffusion coeff. in methanol are determined, and from the results obtained the mol. wt. distribution curve is constructed by a method that is given in detail. It is found that the way in which the form of the distribution function is determined by the progress of the polycondensation reaction is not in accord with Flory's equation (*Chem. Rev.*, **39**, 137 (1945)), which is based on the assumption that reaction proceeds by the condensation of monomer at the ends of growing polymer chains and predicts a very wide scatter of particle sizes. Actually, the distribution is confined to a narrow mol. wt. band, the average mol. wt. increasing as the reaction progresses. The equilibrium state that is ultimately reached can be established also by mixing together fractions of widely differing average mol. wt. obtained from the final soln. of polymer and then subjecting the mixture to the conditions of the polycondensation reaction. It is evident, therefore, that polycondensation is accompanied by chain-rupture reactions, and a theoretical treatment of the process on this basis leads to an equilibrium mol. wt. distribution of the type found experimentally. A. E. S.

Macromolecular Compounds. LII—Interaction of Polyester Molecules. V. V. Korshak and S. V. Vinogradova. *Izvestiya Akad. Nauk S.S.S.R. Otdel. khim. nauk*, 1109–1115 (Nov.–Dec. 1952).

On being heated, polyesters prepared from sebacic acid and hexane-1:6-diol undergo an exchange reaction, the occurrence of which accounts for the low degree of polydispersion in the product of the polycondensation reaction. Thus, when two such polymers of mol. wt. (viscosimetric) 6608 and 1533 respectively are mixed and then heated at 150°c., the degree of polydispersion (measured by comparing the viscosimetric and end-group values of the mol. wt.) falls progressively, equilibrium being reached in about 5 hr.; the viscosimetric mol. wt. of the mixture falls, while the end-group mol. wt. remains const. (const. number of chains). A. E. S.

Dielectric Properties of Polyvinyl Acetals. B. L. Funt and T. H. Sutherland. *Canadian J. Chem.*, **30**, 940–947 (Dec. 1952).

The method and results of the measurement of dielectric dispersion in polyvinyl acetate, and polyvinyl acetal and formal, are given for the frequency range 0·050–100 kc./sec. at 25–135°c. The effects of internal plasticisation on electrical properties are shown by the results. As the size of the substituent group increases from formal to butyral, the dispersion range shifts to lower temp. at a given frequency. Electrical relaxation times and transition temp. were obtained experimentally, and values of enthalpies, free energies, and entropies of activation calculated. A tentative physical picture of the mechanism of dielectric relaxation in these polymers is given. J. W. D.

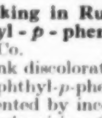
PATENTS

Prevention of Pinking in Rubber containing *NN'*-Di-β-naphthyl-*p*-phenylenediamine. United States Rubber Co. *USP* 2,610,983

Development of pink discoloration in vulcanised rubber containing *s*-di-β-naphthyl-*p*-phenylenediamine as antioxidant can be prevented by incorporating in the rubber composition, before vulcanising, 2:5-di-*tert.*-butylquinol. C. O. C.

Non-staining Antioxidants for Rubber. Firestone Tire & Rubber Co. *BP* 689,589

Non-staining antioxidants for rubber are produced by reaction of 3–4 mol. of an aliphatic aldehyde with 6 mol. of a compound of formula—



(R^1 = subst. or unsubst. Alk of 3–10 C; R^2 = H or subst. or unsubst. Alk of 1–10 C). C. O. C.

Pigmented Silicone Elastomers. T. A. Te Grotenhuis. *USP* 2,610,167

Pigments to the surfaces of which organic groups are linked through Si atoms are used. This may be achieved by separately treating the pigment with a water-hydrolysable or hydroxy-reactive organosilicon compound, but preferably by incorporating the pigment into the elastomer before or during its preparation, condensation, or polymerisation. Most pigments, including carbon black, are suitable for use in this way. C. O. C.

Embossing Thermoplastic Sheets. B. F. Perkins & Son. *USP* 2,609,568

A method of embossing unsupported thermoplastic sheets, e.g. of rubber or vinyl polymers, without formation of wrinkles. C. O. C.

Coated Monofils and other Articles comprising Synthetic Linear Polyesters (VI p. 221).
Physicochemical Properties of the Surface of Aqueous Solutions. III—Mechanical Behaviour of Surfaces of Micellar and Macromolecular Solutions (VIII p. 222).

XIV—ANALYSIS; TESTING; APPARATUS

Simple Microthermostat for use in Colorimetric and other Optical Measurements. W. J. Marshall. J.S.D.C., 202–204 (June 1953).

Sources of Error in the Colorimetric Method of pH Determination in Presence of Textile Auxiliary Products. L. Marcou. *Teintex*, **18**, 3–21 (Jan. 1953).

A study of the effect of anionic, non-ionic, and cationic auxiliary products on cationic and anionic forms of indicators by comparison with measurements obtained with the glass electrode. The colorimetric method was found to be unreliable for the determination of absolute pH; thus measurements on a 0·1% soln. may be in error by > 1 unit of pH. For routine control work the constant error of the indicator at a fixed concn. of product can be experimentally determined. In a theoretical discussion of the tabulated results a distinction is made between interactions of cations with anions, and a "salt" effect connected with the physicochemical properties of surface-active compounds. G. L.

Evaluation of Cellulosic Pulps. K. Heide. *Faserforsch. und Textiltech.*, **3**, 465–477 (Dec. 1952).

The evaluation of the quality of pulp for the rayon industry is discussed, and the use of microscopical examination in conjunction with swelling treatments in ~ 80% phosphoric acid is described in detail; this method gives a rapid and precise assessment of the suitability of the pulp for rayon manufacture. A. E. S.

Detection, by means of Iodine Sorption, of Structural Displacements arising from Mechanical Damage to Fibres. K. Schwertassek. *Faserforsch. und Textiltech.*, **3**, 477–482 (Dec. 1952).

The presence or absence in a textile fibre of a skin or of pores is of little significance for the diffusion of the small molecules of iodine, and the increased absorption of iodine from soln. at the cut ends of cellulose fibres cannot, therefore, be attributed to absence of a diffusion barrier, although this is an important contributing cause of similar differential absorption occurring in dye solutions. The effect is attributed to a disturbance of the cellulose lattice, which is very slight when a sharp cut has been made, but considerable when the fibre has been crushed. However, when the damaged fibre is wetted and dried, iodine sorption returns practically to normal, and it is considered that a recrystallisation process then occurs. Acetate rayon does not show the effect, owing, it is thought, to its lack of crystallinity. Iodine sorption in conjunction with microscopical examination may be used in the diagnosis of the causes of fibre damage. The effect is of importance also in iodine sorption determinations, for it gives rise to appreciable errors when the cellulose is cut up too finely; for accuracy a very sharp knife must be used and the cut length of fibre should be ~ 7 mm. A. E. S.

Determination of the Constitution of Peptides. **I**—F. Wessely, K. Schlögl, and G. Korger. *Sitzungsber. Öster. Akad. Wiss. IIb*, **161**, (8–9), 1156–1174 (1952). **II**—F. Wessely, K. Schlögl, and E. Wawersich. *Ibid.*, **161**, (10), 1426–1438 (1952). **III**—Idem. *Ibid.*, **161**, (10), 1439–1447 (1952).

I—A new method for the identification of the amino acid bearing the free amino group (I) and its neighbour (II) in peptides is described and discussed. It consists in conversion of the peptide into its *N*-carbalkoxy deriv. and treatment with 2 mol. of alkali, when a substituted urea is formed. Boiling HCl produces a hydantoin deriv. built up of I and II, which can thus be identified.

II—The method previously described is tested on further tri- and tetra-peptides. For identification of the amino acid bearing the free carboxyl group (III) in the peptide, the carbalkoxypeptide or the intermediate urea deriv. is converted into the acid chloride and reduced to the alcohol by means of $NaBH_4$. After hydrolysis, the amino-alcohol can be removed and III identified by its absence from a chromatogram.

III—The method for the determination of I and II is made less drastic by the use of alcoholic alkali for producing the substituted urea. Preparation of hydantoins *via* phenylthiocarbonyl deriv. of peptide esters is also investigated. H. E. N.

Stepwise Degradation of Polypeptides from the Carboxyl End. R. A. Boissonnas. *Nature*, **171**, 304 (14 Feb. 1953).

When micro-scale anodic oxidation is applied to *N*-acyl derivatives of polypeptides (0·1% soln. in methanol), the initial amino acid of the acylated peptide (I) is decarboxylated into II and no longer appears on a paper chromatogram of the hydrolysate of II. If II is heated for a short time with dil. aq. HCl, the methoxyalkylamide is hydrolysed to III, which may be isolated and decarboxylated, as above, to IV; after this, when IV is hydrolysed, the spot of the second amino acid is no longer detectable on a chromatogram. Thus, the sequence of amino acids is determined by their successive disappearance on chromatograms. The method is applicable to dinitrophenyl derivatives.

$$\mathrm{X{\cdot}NH{\cdot}CHR^2{\cdot}CO{\cdot}NH{\cdot}CHR^1{\cdot}COOH}$$
$$\text{(I)}$$
$$\rightarrow \mathrm{X{\cdot}NH{\cdot}CHR^2{\cdot}CO{\cdot}NH{\cdot}CHR^1{\cdot}O{\cdot}CH_3 + CO_2}$$
$$\text{(II)}$$
$$\rightarrow \mathrm{X{\cdot}NH{\cdot}CHR^2{\cdot}COOH + NH_3 + R^1{\cdot}CHO + CH_3OH}$$
$$\text{(III)}$$
$$\rightarrow \mathrm{X{\cdot}NH{\cdot}CHR^2{\cdot}O{\cdot}CH_3 + CO_2}$$
$$\text{(IV)}$$

J. W. B.

Paper Electrophoresis of Polyglutamyl Peptide. R. E. Strange and N. Harkness. *Nature*, **171**, 77–78 (10 Jan. 1953).

A technique is described for detecting polyglutamyl peptide by paper electrophoresis. Artificial mixtures of the peptide and complete proteins give distorted results, which suggest interaction between protein and polyglutamyl peptide, a factor which should be considered when electrophoresis is used to separate unknown mixtures. J. W. B.

Colour in Electron Microscopy. G. E. Donovan and E. Stafford. *Nature*, **170**, 1126–1127 (27 Dec. 1952).

Two or more electron micrographs of the specimen are taken at different accelerating voltages, selected to give the desired contrast. The images are each tagged in a visible colour, and are superimposed to give a colour electron micrograph in which the different colours represent varying distribution of material in the specimen absorbing or scattering at the voltages selected. A pseudo depth effect may be obtained by suitable choice of colours. B. M.

Shadow Microscopy for Measuring Height. S. Tolansky. *Nature*, **171**, 564–566 (28 March 1953).

A technique is described whereby magnifications in height of ca. 10,000 are obtained with a microscope magnification of 500. J. W. B.

Control of Azotol A Solutions. N. K. Mokoshev and Yu. P. Kalachina. *Tekstil. prom.*, **12**, 44 (Oct. 1952).

Details are given of the control of Azotol A (= Naphtol AS) baths in the works laboratory by titration with solutions of Diazols (= Fast Colour Salts). A. E. S.

Laboratory Sizing Apparatus. L. Pamaud and J. Chabert. *Bull. Inst. Text. France*, (36), 27–30 (Dec. 1952).

The apparatus described is claimed to be suitable for the small-scale study under reproducible conditions of the variable factors affecting the industrial sizing process. Hot air is used for drying. G. L.

Colour Reactions of α-Ionone and of 5-Oxo-α-ionone with Alkali (IV p. 212).

Sesquiterpenes and Azulenes. CV—Polarographic Reduction of Azulenes—I (IV p. 212).

Air Flow Method of Measuring the Specific Surface of Jute. II—Chemically Treated Fibres (VI p. 218).

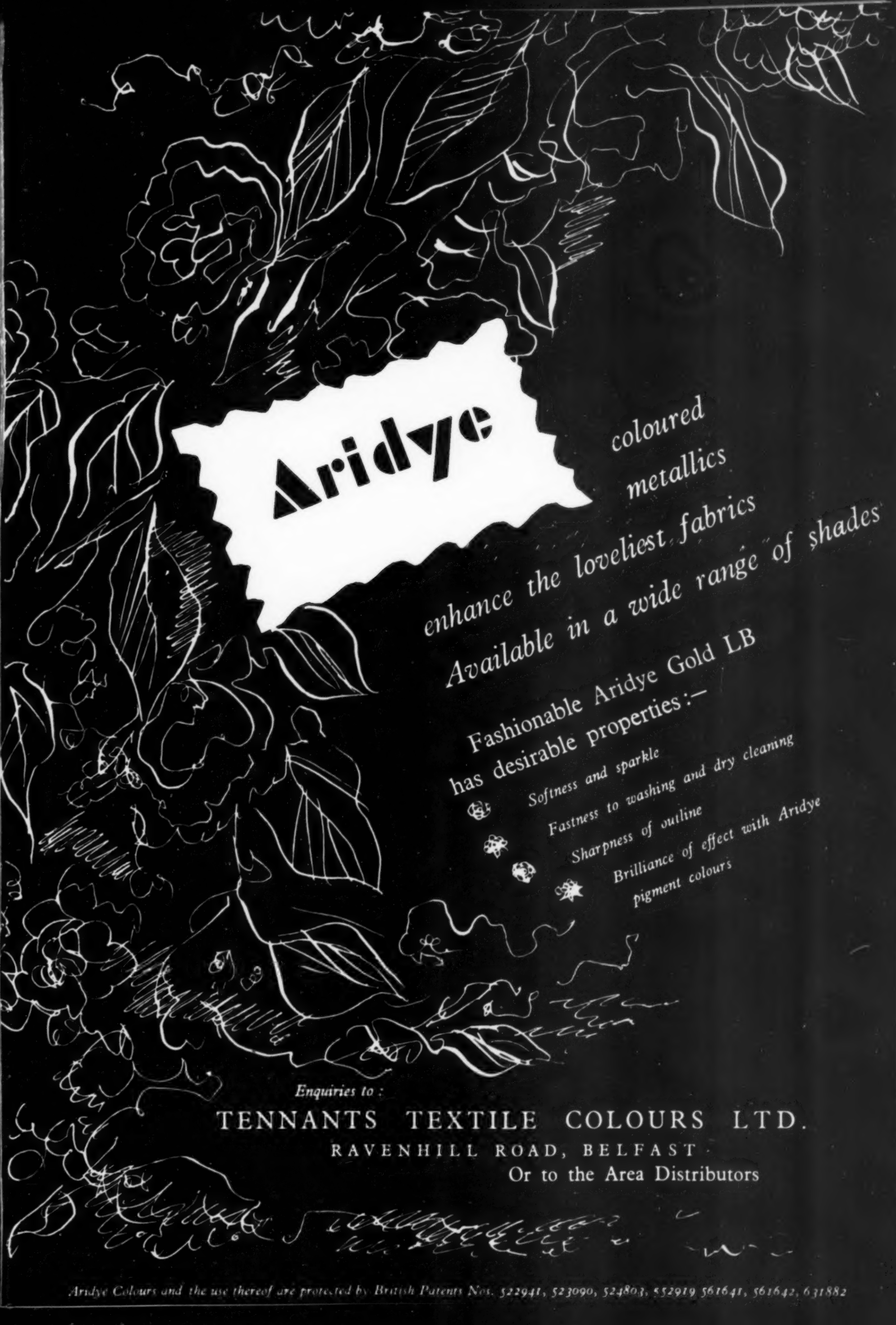
Mechanism of the Absorption of Inhaled Carbon Disulphide, and its Location in the Human Body (VI p. 219).

Stress Relaxation of Fibrous Materials. I—Instrumentation and Preliminary Results (VI p. 219).

Apparent Degradation of Wool by Diazomethane Solutions (VI p. 219).

Concentration-Viscosity Curves as an Index of the Cross-linking of Perlon (VI p. 220).

Mobility of Oil Droplets, Interfacial Tension Measurements, and Gegenion Adsorption in Soap Solutions (VII p. 221).


Aridye
coloured
metallics
enhance the loveliest fabrics
Available in a wide range of shades
Fashionable Aridye Gold LB
has desirable properties:—
Softness and sparkle
Fastness to washing and dry cleaning
Sharpness of outline
Brilliance of effect with Aridye pigment colours
Enquiries to:
TENNANTS TEXTILE COLOURS LTD.
RAVENHILL ROAD, BELFAST
Or to the Area Distributors
Aridye Colours and the use thereof are protected by British Patents Nos. 522941, 523090, 524803, 552919 561641, 561642, 631882

SITUATIONS VACANT AND WANTED *etc*

Replies may be addressed "Box —, SOCIETY OF DYERS AND COLOURISTS," DEAN HOUSE, 19 PICCADILLY, BRADFORD, 1, YORKS., where all communications relating to these Advertisements, which are treated in strict confidence, should be addressed.

The Publications Committee is prepared to receive Advertisements relating to SITUATIONS VACANT, SITUATIONS WANTED, or MISCELLANEOUS ITEMS for insertion on this page of the Journal. Advertisements of Situations Wanted are gratis to individual members, but must not exceed twenty-four words in length.

All inquiries relating to Advertisements in the Journal should be addressed to THE GENERAL SECRETARY, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD, 1, YORKS.

SITUATIONS VACANT

APPLICATIONS are invited from Textile Chemists for a progressive position in a large manufacturing firm in Lancashire. Applicants should be able to organise testing and do research. Initial salary will depend on the qualifications and experience of the successful candidate. The company operates a superannuation scheme. Please apply in writing to Box V15.

G. & W. N. HICKING, Queen's Road, Nottingham, require an assistant chemist keen on process and chemical control work. Good knowledge of modern bleaching, dyeing and finishing techniques is desirable. Salary commensurate with experience and qualifications.

SITUATIONS VACANT *continued*

WANTED for Middle East a fully qualified Chemist/Colourist/Printer, aged 45–60 of wide experience for top managerial position with appropriate salary and accommodation. Previous experience abroad desirable. Applications will be treated in strict confidence and should give brief details of post held. Box V16

SITUATIONS WANTED

DYER—2 years' experience dyeing nylon, Final City and Guilds Certificates, desires post home or abroad. Box W513

MEMBERS AND JUNIOR MEMBERS

Persons desirous of joining the Society as Ordinary Members or Junior Members may obtain Application Forms from the General Secretary, or from the Honorary Secretary of any Section of the Society

NEW MEMBERS

Appleyard, J. N., St. Briac, 979 Scott Hall Road, Moortown, Leeds

Barbero, J. Alameda, Defensores de Oviedo No. 6, Burgos, Spain

Booth, H. G., "Holmdene", 187 Parkside, Darlington

Engez, S., Akaretler, Yeni Yol No. 12, Besiktas, Istanbul, Turkey

Jones, K. W., 55 Beverly Road, Fallowfield, Manchester 14

Jowett, F., "Corrour", 8 Nab Wood Mount, Shipley, Yorkshire

Parrott, A. E., 57 Ludbrook Avenue, Caulfield, Victoria, Australia

Peach, F., 18 Church Street, Oswaldtwistle, Lancs.

Schaumann, C. F., E.I. du Pont de Nemours & Co. Inc., Wilmington, Delaware, U.S.A.

Smith, E., 80 Fair View Road, Bacup, Lancs.

Taylorson, R. B., Congdon Hill Road, Saunderstown, Rhode Island, U.S.A.

Turner, J. T., 27 Hilda Avenue, Tottington, near Bury, Lancs.

Walshaw, C. L., Messrs Walshaw Drake & Co. Ltd., Rosemary Dyeworks, Brighouse, Yorkshire

Zimmerman, C. L., American Cyanamid Company, Calco Chemical Div., Bound Brook, New Jersey, U.S.A.

NEW JUNIOR MEMBER

McDowell, D. J., 68 Primrose Bank, Oldham, Lancs.

ADDRESSES WANTED

Brun, J. S., formerly of P.O. Box 20, Bergen, Norway

Clarke, J. A., formerly of 38 St. Pauls Road, Manningham Lane, Bradford

Crummett, K., formerly of 14 St. Austell Road, Manchester 16

Evelbauer, H. L., formerly of Friedrichsster F., Marburg (16), Hessen, U.S. Zone, Germany

Faulkner, J., formerly of 53 Garden Village, Muckamore, Co. Antrim, Northern Ireland

Freeman, S. R. T., formerly of 8 The Avenue, Blaby, near Leicester

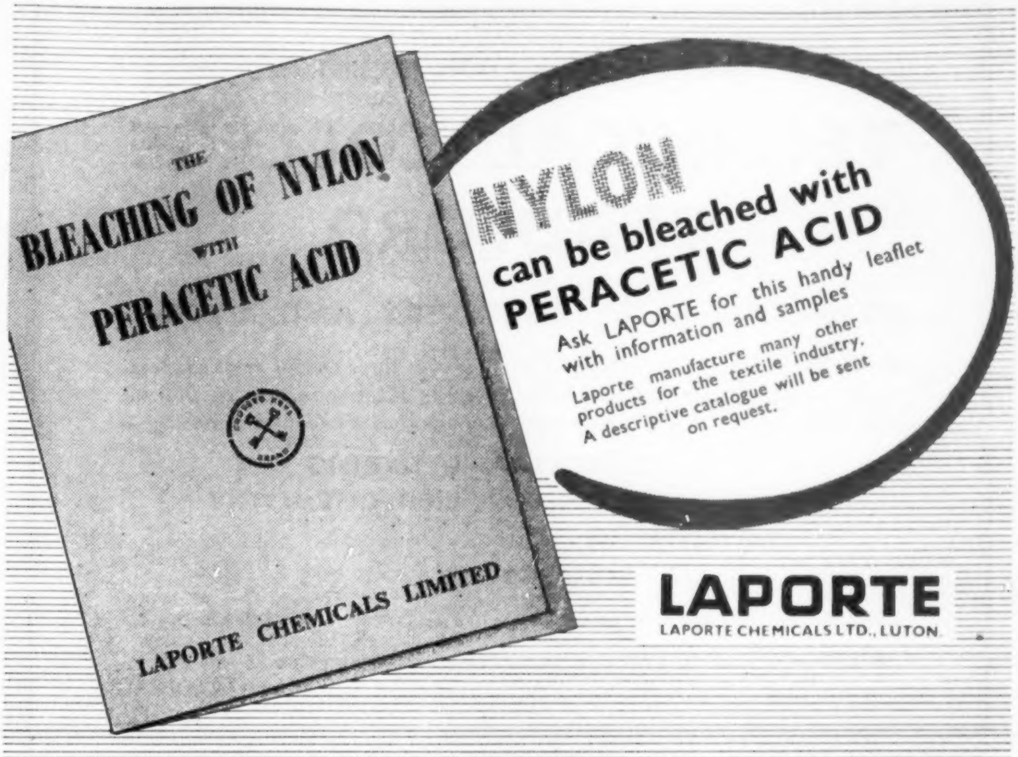
Holt, J., formerly of "Greystones", St. Martin's Road, Marple, Cheshire

Kazan, R. E., formerly of c/o Howards & Sons Ltd., 815 Castle Building, 1410 Stanley Street, Montreal, P.Q., Canada

Lowe, R., formerly of 17 Ashdown Avenue, Leicester

Sykes, J. H., formerly of 75 Hill Crescent, Howden Clough, Birstall, near Leeds

Walton, A., formerly of 8 Knights Avenue, Teltenhall, Wolverhampton


THE
BLEACHING OF NYLON
WITH
PERACETIC ACID
LAPORTE CHEMICALS LIMITED
NYLON
can be bleached with
PERACETIC ACID
Ask LAPORTE for this handy leaflet
with information and samples
Laporte manufacture many other
products for the textile industry.
A descriptive catalogue will be sent
on request.
LAPORTE
LAPORTE CHEMICALS LTD., LUTON

Notice to Authors of Papers

The MSS. of all papers communicated to or read before the Society become the property of the Society. They should be addressed to the Editor, Society of Dyers and Colourists, 19 Piccadilly, Bradford 1. Authors must not allow their papers to be published elsewhere before they have appeared in the Society's *Journal*. Should prior publication take place without the sanction of the Publications Committee, the paper will be printed only as an abstract or summary.

Manuscripts submitted for publication in the *Journal* should be typewritten (double spacing) on good-quality paper, using one side of the paper only and leaving a margin at least 1 in. wide on the left-hand side. The time taken in refereeing papers (both lectures and communications) will be reduced to a minimum when authors submit two copies of the typescript.

In view of the high costs of publication, it is essential that authors should be as concise as possible. When experimental procedure has already been published, a literature reference to the paper containing the details is sufficient, whilst well known experimental methods should be described very briefly.

Introductory paragraphs describing the aims of the investigation and the method of attack are desirable, and should be followed by the experimental results and their discussion. There should be a brief summary for insertion at the beginning of the paper. References to the literature should be numbered consecutively, using superscript numbers without brackets immediately following the text words or author's name to which they refer.

The list of references should be given at the end of the manuscript and the abbreviations used should be, as far as possible, those given in the "List of Periodicals Abstracted" included at the end of the Index to the preceding year's *Journal*. Reference numbers in this list should be neither enclosed in brackets nor followed by full-stops. As far as possible throughout the manuscript the abbreviations listed in the Jan. 1950 issue (p. 54) should be used. Tables should be numbered consecutively in Roman numerals and Figures in Arabic numerals.

The number of figures and graphs should be kept as low as possible, and data should be presented in the form of either tables or graphs, not both. Drawings should be carefully prepared, preferably in Indian ink, on plain white drawing paper or, preferably, Bristol board. In graphs, the frame and actual curves should be ruled and inked more heavily than any co-ordinate lines, and the latter should not be close together as in ordinary graph paper. Experimental points should always be given, and where several graphs appear in a single Figure clear means of differentiation must be adopted. All numbers and legends are set up in type by the printer, and authors should therefore indicate them lightly in pencil.

Twenty-five free copies of a reprint are supplied to the author of an original paper published in the *Journal*, or fifty free copies are supplied when there are two or more authors, and a further number may be purchased from the Society at the rates given below.

REPRINTS OF LECTURES AND COMMUNICATIONS

Reprints of all lectures and communications are available after publication to members and non-members of the Society. The charges (postage included) are as follows— Single copies 2s. 6d. each; per dozen copies up to and including 8 pages, 12s. 6d., and for papers occupying more than 8 pages of the *Journal*, 17s. Orders should be addressed to "The Society of Dyers and Colourists, 19 Piccadilly, Bradford 1". They can be accepted only if accompanied by remittance and if received immediately after publication of the paper.